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1. *Relations between Acidity and Tautomerism. Part III. The Nitro-group and the Nitronic Esters.*

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THE methods, deductions, and terminology developed in the previous communications of this series (Part I, Arndt and Martius, *Annalen*, 1932, **499**, 228; Part II, Arndt and Scholz, *ibid.*, 1934, **510**, 62) are applied in this paper to the group $CH \cdot NO_2$. The acidity-promoting action (acidification) of nitroxyl is stronger than that of the substituents hitherto studied, as is shown by its effect on hydroxyl in the simplest example ($HO \cdot NO_2$). The degree of acidity produced in a hydrocarbon residue by the introduction of *one* nitro-group is, empirically speaking, sufficient to endow the substance with the property of solubility in aqueous alkalis, whereas *two* sulphonyl groups or *three* carbethoxy-groups are necessary to produce this effect.

The following questions arise : (1) Is this empirical acidity due only to the acidification of the CH by the nitro-group, or to a previous progressive transformation into a more acidic hydroxyl form? (2) What is the constitution of the hydroxyl form, if any? In the case of the SO_2 group, the answer to the first question has been shown (Arndt and Martius, *loc. cit*) to be, that the action of sulphonyl is purely acidifying without tautomerism. This is in harmony with the electronic formula (I), in which there is no double bond. The electronic formula (II) of the nitro-group, however, shows one of its oxygen
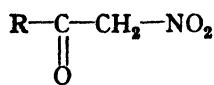

atoms to be bound by a double bond which makes the nitro-group analogous to carbonyl rather than to sulphonyl and it might therefore be capable of electromeric change and of acting as a partner in conjugation.

It is well known, thanks to Hantzsch, that certain arylnitromethanes yield, on acidification of their alkaline solutions, solid *aci*-forms (nitronic acid), which are much more acidic than the normal forms, and from which, furthermore, they are sharply distinguished by intense colour reactions with ferric chloride, and unsaturation towards bromine. Unlike the enolic modifications of many β-dicarbonyl compounds, these nitronic acids are unstable and soon revert entirely to the normal form. No spontaneous change of a normal nitro-compound to the free *aci*-form has been observed. The existence of the nitronic acids, therefore, gives no complete answer to question (1), although it is clear that the salts of the mononitrated hydrocarbons have the electronic system of the nitronic acids.

K. H. Meyer (*Ber.*, 1914, **47**, 2380) concludes that nitro-ketones of the type (III) enolise appreciably, although to a less extent than β-ketonic esters, and that this enolisation involves the carbonyl (IV) rather than the nitro-group. This suggests that the enolising tendency of the nitro-group is less than that of keto-carbonyl, but that the nitro-group is implicated in the full conjugated system. The acidifying action of the nitro-group cannot

alone explain such enolisation of the keto-group beca␢␢␢␢␢sulphonyl ketones are non-enolising (Arndt and Martius, *loc. cit.*). The effect of ␢␢␢␢n–oxygen double bond is apparent here, although to a less extent than in the case ␢␢␢␢yl, even ester carbonyl.
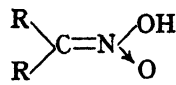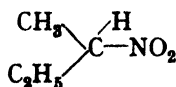
R—C—CH$_2$—NO$_2$ (with ‖O below C)   R—C=CH·NO$_2$ (with OH below) $\begin{array}{c}R\\R\end{array}$C=N$\begin{array}{c}OH\\O\end{array}$

(III.)   (IV.)   (V.)

$\begin{array}{c}CH_3\\C_2H_5\end{array}C\begin{array}{c}H\\NO_2\end{array}$ $\begin{array}{c}CH_3\\C_2H_5\end{array}$C—N$\begin{array}{c}O\\O\end{array}$ $\begin{array}{c}CH_3\\C_2H_5\end{array}$C—N$\begin{array}{c}O\\OH\end{array}$
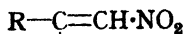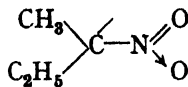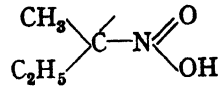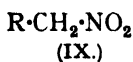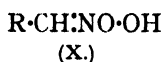
(VI.)   (VII.)   (VIII.)

With regard to the constitution of the nitronic acids and their salts, the three-membered ring formula tentatively suggested by Hantzsch (*Ber.*, 1896, **29**, 699, 702, 2251) was later abandoned by Hantzsch himself and for very good reasons (*Ber.*, 1912, **45**, 89, footnote 1). Since then the generally accepted formula has been (V), analogous to the enols of carbonyl compounds.
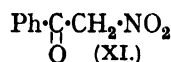
Kuhn and Albrecht (*Ber.*, 1927, **60**, 1297) found that on treating a methanol solution of the optically active *sec.*-nitrobutane (VI) with sodium methoxide, the optical activity was preserved. This was corroborated by Shriner and Young (*J. Amer. Chem. Soc.*, 1930, **52**, 3332) in the case of 2-nitro-*n*-octane. As (V) contains no centre of asymmetry, Kuhn and Albrecht ascribe the structure (VII) to the anion in which the unshared pair of electrons on the carbon atom is supposed to function as a fourth substituent, analogous to the optically active sulphoxides and sulphinic esters of Phillips. To the *aci*-form, the structure (VIII) is ascribed, *i.e.*, the proton which is added to the anion (VII) on acidification becomes temporarily attached to the singly bound oxygen atom, which is available in the nitro-group in any case, and from this unstable condition returns to the unshared carbon electrons. The Kuhn–Albrecht formula implies that salt formation in the mononitrated hydrocarbons consists exclusively in the removal of the proton from the carbon, without any electronic change (cf. Kuhn and Albrecht, *loc. cit.*, footnote 19) and that the tautomerism of the nitro-group is purely prototropic. This would suggest that the double bond of the nitroxyl is incapable of electromeric changes, leading to the conclusion that the nitro- and the sulphonyl group are practically analogous. One would, therefore, expect the behaviour of suitably constituted analogous nitro-sulphonyl compounds towards diazomethane to be comparable, *i.e.*, sufficiently acidic normal nitro-compounds containing no aldehydo- or keto-carbonyl should be capable of *C*-methylation. Our experiments, however, give evidence to the contrary.

R·CH$_2$·NO$_2$ R·CH:NO·OH   Ph·C·CH$_2$·NO$_2$ (with ‖O below C)

(IX.)   (X.)   O   (XI.)

NO$_2$·CH$_2$·C·OEt (with ‖O below C)   O:C(OMe)·CH(NO$_2$)·CO·OMe $\overset{O}{\underset{O}{C_6H_4Me\cdot S\cdot CH_2\cdot NO_2}}$
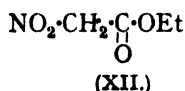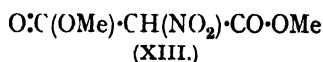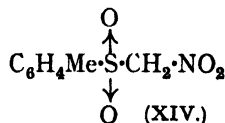
(XII.)   (XIII.)   (XIV.)

The following compounds have been investigated: Phenylnitromethane (IX, X; R = Ph), *p*-bromophenylnitromethane (IX, X; R = C$_6$H$_4$Br), ω-nitroacetophenone (XI), ethyl nitroacetate (XII), methyl nitromalonate (XIII), and *p-toluenesulphonylnitromethane* (XIV). The last compound has been prepared as an example of a type in which the methylene group carrying the nitro-group is very strongly acidified, but in which no conjugated system is possible. This sulphone nitromethane, a new type, was prepared by the introduction of the nitro-group into the sulphides C$_6$H$_4$Me·S·CH$_2$·CO·R (R = CH$_3$ or C$_6$H$_5$), by ethyl nitrate and sodium ethoxide, followed by oxidation with hydrogen peroxide ; the acyl group is eliminated during the reactions.

The two nitronic acids (X), as expected, react vigorously with diazomethane to give the

nitronic esters. The corresponding normal nitro-compounds (IX), the solutions of which give none of the reactions of the nitronic acids, show no visible reaction with diazomethane, but are nevertheless slowly transformed into the same nitronic esters as obtained from the *aci*-forms. In these cases it would be possible to assume that during the long duration of the reaction the whole of the starting material has gradually undergone spontaneous isomerisation into the *aci*-form, the equilibrium amount of which is too small to be detected by ferric chloride, etc., but which, on account of its strong acidity, can react with diazomethane. Such an assumption, however, becomes untenable in the cases of (XII) and (XIV). These compounds, too, give no enolic reactions, but they react vigorously with diazomethane, yielding also nitronic esters. Considering the difference between the sulphonyl ketones (which do not enolise) and the β-ketonic esters (which enolise considerably), then, if the reaction of (XIV) were due to spontaneous desmotropy, the equilibrium amount of nitronic acid in (XII) ought to be detectable by ferric chloride. The authors, therefore, consider the formation of nitronic esters from (XII) and (XIV) to be analogous to the formation of enolic esters from sulphonyl ketones, *i.e.*, due to the mechanism described in Part I of this series as " indirect methylation." It also seems probable that the same mechanism applies in the case of (IX). The electronic conditions for this mechanism, which, in the case of a keto-carbonyl, are fulfilled only by the presence of a sulphonyl group in the β-position, are fulfilled by the nitro-group as such, with regard both to the polarity of the double bond and to the necessary mobility of a neighbouring proton. Nitromalonic ester (XIII) shows, in alcoholic solution, a feeble enolic reaction which, after the experience with toluenesulphonylmalonic ester and methanetricarboxylic ester (Part I), is probably due to a small enolisation of the ester carbonyl. Nevertheless diazomethane, reacting vigorously, yields almost quantitatively and under all conditions the nitronic ester; the indirect methylation of the nitro-group prevails. ω-Nitroacetophenone (XI) shows a much stronger enolic reaction due to the enolisation of the carbonyl (see above); the reaction product with diazomethane is an oil which contains much nitronic ester, and is probably a mixture of about $\frac{2}{3}$ nitronic ester and $\frac{1}{3}$ enolic ester. This result would be easily explained by the competition between the indirect methylation of the nitro-group and the methylation of the enol.

It follows that the behaviour of the nitro-group is entirely different from that of the sulphonyl group, and is similar to that of carbonyl under corresponding conditions of polarity. It shows either tautomerism or indirect methylation. The latter implies an addition reaction of the nitrogen—oxygen double bond, which, in its turn, depends on a tendency for electromeric changes. In both cases there is a disagreement with the deductions from the Kuhn–Albrecht formulæ (VII) and (VIII). Tertiary and aromatic nitro-compounds do not exhibit addition reactions with diazomethane, but it can be assumed that the addition is reversible, and therefore does not lead to a permanent change unless a mobile proton interferes. Aromatic polynitro-compounds react with diazomethane (Heinke, *Ber.*, 1898, **81**, 1399) and it is noteworthy that the same compounds give addition reactions with many other reagents.

With regard to question (1) (p. 1), the acid character of (XII) and (XIV) must be evinced at the methylene group, and the feeble enolisation of (XIII) is shown to contribute little towards the observed acidity. The formation of salts of mononitrated hydrocarbons such as nitromethane and (IX) in aqueous alkaline solution need not be consequent on previous isomeric change to the *aci*-form, even if this were the case in the slow reaction with diazomethane. Since the action of hydroxyl ion, unless it is an addition reaction, consists in the removal of a proton, and since the desmotropic changes in question are considered to be prototropic, it is difficult to conceive that the proton, after leaving the carbon through the influence of alkali, should become temporarily and loosely attached to the oxygen of the nitro-group before uniting with hydroxyl ion. The slowness of the dissolution of such nitro-compounds (as compared with XII—XIV) in aqueous alkali need not be due to a slow tautomeric process, but can be attributed to the weakness of the acidity of the methylene. This weakness does not show itself, as it usually does, in the incomplete formation of a salt (hydrolytic equilibrium), because the process is irreversible; as soon as the proton is removed from the carbon, the resulting electronic system changes to the

nitronic state (corresponding to V), which is far less prone to recapture the proton. The Kuhn formula (VII), on the contrary, does not account for this stability towards hydrolysis.

The anions of nitro-compounds containing carbonyl (XI—XIII, etc.) would be expected to be enolic, rather than nitronic, owing to the greater " enotropic effect " of carbonyl, or " in between the two " (cf. Arndt, *Ber.*, 1930, **63**, 2963). The salts of (XIII) are known to yield the *C*-methyl derivative with methyl iodide (Beilstein, IV edition, **2**, 597), as do enolic salts; the silver salt of (XII) gives with methyl iodide at least in part the *C*-methyl product (Steinkopf, *Annalen*, 1923, **434**, 21), whereas the alkaline solution of (IX) yields the nitronic ester with methyl sulphate (see below).

The nitronic esters from bromophenylnitromethane, and from nitromalonic ester (XIII) are crystalline solids in the pure state; the rest are liquids, diagnosed by means of alkoxyl estimations. All these nitronic methyl esters are characterised by the violent decomposition which occurs at 70—90° with evolution of formaldehyde in all cases except (XIV). This property has been ascribed to the whole class by Nef (*Annalen*, 1894, **280**, 286), who, however, did not isolate any of them. Bamberger (*Ber.*, 1901, **34**, 589) obtained from phenylazonitromethane with diazomethane a crystalline nitronic ester showing the same property. This seems to be the only authentic nitronic ester hitherto described. Hantzsch (*Ber.*, 1907, **40**, 1541) describes a " perfectly stable " nitronic ester obtained from the silver salt of phenylcyanonitromethane with methyl iodide, and attributes this stability to the presence of two negative radicals. In view of the instability of the nitronic ester from (XIII), and considering that Bamberger (*loc. cit.*, p. 590) obtained from the salt of phenylazonitromethane with methyl iodide an *N*-methyl derivative, the compound of Hantzsch, which has not been proved to contain methoxyl, may be an *N*-methyl derivative. Steinkopf (*Annalen*, 1923, **434**, 29) claims to have obtained the nitronic ester of (XIII) as the main product of the action of methyl iodide on the silver salt. This product is described as boiling at 84°/2·5 mm. and no decomposition with evolution of formaldehyde is mentioned. The product obtained from (XIII) with diazomethane, giving the correct alkoxyl value, has quite different properties. Auwers (*Ber.*, 1924, **57**, 456) described the nitronic ester of phenylnitromethane as being obtained from the alkaline solution of the latter on treatment with methyl sulphate, and as distilling at 117°/10 mm. On repeating this experiment, we found that the product was actually the nitronic ester, but we were unable to distil it unchanged; the fraction b. p. 117°/10 mm. contained no methoxyl and was a mixture of benzaldehyde and other products.

The nitronic ester from (XIV) also decomposes at 80—90°, but according to the equation $C_7H_7 \cdot SO_2 \cdot CH{:}NO \cdot O \cdot CH_3 = C_7H_7 \cdot SCN + CO_2 + 2H_2O$. It is remarkable in this case that not only the nitrogen but the sulphone group is reduced, in favour of a complete oxidation of the methyl.

The nitronic esters are more or less readily attacked by strong aqueous acids and by aqueous alkali. In this case, however, the methyl is not oxidised but is eliminated in the form of methanol. The original nitro-compound has never been recovered from a nitronic ester, as saponification is accompanied by a reduction of the nitronic group with corresponding oxidation of the reagent (hydriodic acid) or even of the carbon atom attached to nitrogen.

On treatment of the nitronic ester from (XIII) with cold concentrated hydrochloric acid, nitrogen trioxide and other products not yet identified were produced. The action of cold 2*N*-sodium hydroxide is comparatively slow, thereby excluding the possibility of the compound being a keten-acetal (compare the behaviour of the keten-acetal from the methane-tricarboxylic ester, Part I); the nitronic ester dissolves within about 5 minutes, to yield methanol, carbonate, and fulminate. The nitronic ester from (XII) is immediately attacked by concentrated hydrochloric acid, even at − 10°, and is transformed, with evolution of heat, into chloro-oximinoacetic ester (whereas Steinkopf, *loc. cit.*, had to evaporate his ester with concentrated hydrochloric acid, and states that it is transformed into *iso*nitrosoacetic acid); cold 2*N*-sodium hydroxide yields, also exothermically, the so-called " bis-anhydro-nitro-acetic ester " described by Scholl (*Ber.*, 1901, **34**, 868, 876), which is a dimerisation product of oxalic ester nitrile oxide, different from furoxandicarboxylic ester.

These vigorous reactions with acids are exhibited only by the nitronic esters containing carbonyl. The same esters on treatment with cold azeotropic hydriodic acid release iodine :

the ester from (XII) gives two atoms of iodine, the ester from (XIII) between four and five atoms, which is explained by the entire fission of the nitronic group with strong acids. The fact that the product from (XI) (which also contains one carbonyl) and diazomethane releases only 1·3 atoms of iodine instead of two, with partial recovery of the original nitro-ketone, leads us to the assumption that it contains about $\frac{1}{3}$ of enolic and $\frac{2}{3}$ of nitronic ester.

The nitronic esters from (IX) to (X) do not release appreciable amounts of iodine from cold azeotropic hydrogen iodide; they are attacked by concentrated hydrochloric acid only on warming and are transformed into the corresponding diaryl oxdiazoles. The nitronic ester from (XIV) gave with hot acids and alkali, tarry products which could not be purified.

The original nitro-compounds are far more stable towards acids, alkali and reduction by hydriodic acid under the same conditions. This difference leads again to the conclusion that the electronic structure of the nitronic group is different from that of the nitro-group, as expressed by formulæ (II) and (V). It seems desirable to ascertain whether the conditions of experiment used by Kuhn and Shriner and their collaborators lead to the removal of a proton; this investigation is being carried out, independently of the present authors, by Dr. Weissberger in this laboratory.

EXPERIMENTAL.

p-Bromophenylnitromethane (IX, R = C_6H_4Br).—This was prepared according to Wislicenus and Elvert (*Ber.*, 1908, **41**, 4121) and Scholtze (*Ber.*, 1896, **29**, 2253); m. p. 60°. It was converted into the *aci-p*-bromophenylnitromethane by dissolution in 2*N*-sodium hydroxide, and acidification of the filtered ice-cold solution with 2*N*-sulphuric acid. The *aci*-form may be recrystallised from a large volume of light petroleum, forming white needles, m. p. 90°, but even the crude precipitated compound has m. p. 89—90°.

The Methyl Ether of aci-p-*Bromophenylnitromethane.*—(a) *Methylation of* aci-p-*bromophenyl-nitromethane.* A solution of dried precipitated *aci-p*-bromophenylnitromethane (1 g.) in anhydrous ether (50 c.c.) was treated with an ethereal solution of diazomethane (from 5 g. of nitrosomethylurea), and 15 minutes after the vigorous reaction and gas evolution had ceased the solution was filtered, and the solvent removed under diminished pressure at 15°. The viscous yellow residue, which solidified on cooling and scratching, was crystallised from the minimum of methanol at − 20°, and again from light petroleum, forming white needles, m. p. 65° (Found : C, 42·0; H, 3·6; MeO, 12·9.* $C_8H_8O_3NBr$ requires C, 41·7; H, 3·5; 1MeO, 13·5%).

(b) *Methylation of* p-*bromophenylnitromethane.* *p*-Bromophenylnitromethane (20 g.) was treated in anhydrous ethereal solution with diazomethane (from 40 g. of nitrosomethylurea). Evolution of gas was not more rapid than that which normally occurs in diazomethane solutions, and the reaction mixture was kept for 3 days. The solvent was removed under diminished pressure, and the oily product was seeded with the nitronic ester produced by method (a); it then solidified, and after crystallisation from methanol, and later from light petroleum, yielded white needles (7 g.), m. p. and mixed m. p. with the ester produced by method (a), 65°.

Decomposition of the Nitronic Ester.—(a) When plunged into a bath at 80°, the ester underwent almost explosive decomposition and evolved formaldehyde, which was recognised by passage into a solution of *o*-nitrophenylhydrazine in *N*-hydrochloric acid, a thick orange precipitate of formaldehyde-*o*-nitrophenylhydrazone being produced : long orange needles from methanol, m. p. and mixed m. p. with an authentic specimen, 84°. This method was used throughout for the detection and proof of the presence of formaldehyde in decomposition products of the nitronic esters.

The residues, after decomposition of the nitronic ester, were dissolved in dilute caustic soda solution, filtered, and acidified, yielding a white solid which crystallised from petroleum (b. p. 100—120°) in needles, m. p. 110°. This substance contained nitrogen, and showed the m. p. 110° given in the literature for *p*-bromobenzaldoxime (*Ber.*, 1897, **30**, 1899). (b) The nitronic ester was boiled for 5 minutes with a large excess of hydrochloric acid (*ca.* 15%) and the semi-solid residue obtained on cooling was collected, dried, and crystallised from *n*-butyl alcohol and then from ethyl acetate, forming white needles, m. p. 181°. This substance is considered to be 3 : 5-*di*-p-*bromophenyl*-1 : 2 : 4-*oxadiazole*, the structure being supported by the analogous formation of 3 : 5-diphenyl-1 : 2 : 4-oxadiazole from the nitronic ester related to phenylnitromethane (q.v.) (Found : C, 44·7; H, 2·3; N, 7·3; *M*, cryoscopic in camphor, 383. $C_{14}H_8ON_2Br_2$

* All alkoxyl determinations were carried out by the method of Viebӧck (*Ber.*, 1930, **63**, 2818).

requires C, 44·2; H, 2·1; N, 7·4%; *M*, 380). On prolonged heating with hydrochloric acid, the nitronic ester yields *p*-bromobenzoic acid, m. p. and mixed m. p. with an authentic specimen, 251°, also characterised by the preparation of the methyl ester, m. p. and mixed m. p. 79°.

The nitronic ester yields no iodine when treated with cold colourless azeotropic hydriodic acid.

The Methyl Ether of aci-*Phenylnitromethane.*—(a) aci-Phenylnitromethane (2·5 g.) in dry ether (50 c.c.) was cautiously treated with a dry ethereal solution of diazomethane (from 10 g. of nitrosomethylurea). There was a vigorous reaction and gas evolution, and the solution was kept for 15 minutes, and the ether then removed under diminished pressure; the residual yellow oil would not crystallise and methoxyl was therefore estimated after prolonged drying in a vacuum desiccator (Found : MeO, 17·3. $C_8H_9O_2N$ requires 1MeO, 20·5%); the low value was expected, as the ester slowly decomposes even in the cold. (b) Phenylnitromethane (2 g.), methylated during 3 days with diazomethane (from 10 g. of nitrosomethylurea), yielded a yellow oil identical in properties with that produced by method (a) (Found in dried material : MeO, 17·1%). The nitronic ester is insoluble in hot alkalis, gives no ferric reaction, absorbs only a little bromine in alcoholic solution, and does not oxidise hydriodic acid.

Decomposition of the nitronic ester. (a) When plunged into a bath at 85°, the ester decomposed suddenly with evolution of formaldehyde. When the ester was heated slowly from room temperature to 100°, the decomposition was slow and benzaldehyde was recognised in the gaseous products (*o*-nitrophenylhydrazone, m. p. and mixed m. p. 185°). The decomposition also took place at room temperature, and the benzaldehyde formed in 3—4 hours was again recognised as its *o*-nitrophenylhydrazone. (b) The nitronic ester was boiled for 5 minutes with hydrochloric acid (*ca.* 15%); the semi-solid product crystallised from methanol in long white needles, m. p. 108°, undepressed in admixture with authentic 3 : 5-diphenyl-1 : 2 : 4-oxadiazole prepared from benzamideoxime according to Schulz (*Ber.*, 1885, **18**, 1081) (Found : C, 75·2; H, 4·6; N, 12·7. Calc. for $C_{14}H_{10}ON_2$: C, 75·6; H, 4·5; N, 12·6%).

Repetition of an Experiment of von Auwers (*Ber.*, 1924, **57**, 456).—Methyl sulphate (12 g.) was added to a cold solution of phenylnitromethane (10 g.) in the minimum of aqueous 2*N*-sodium hydroxide and the whole was shaken vigorously for 30 minutes; a little more caustic soda was then added to preserve an alkaline reaction, and the shaking was continued for a further 30 minutes. The excess of methyl sulphate was then decomposed with ammonia, the heavy oil taken up in ether, washed with dilute acid and with water, and dried, and the solvent removed at a low temperature. The residual oil exhibited the properties of the nitronic ester described above; it decomposed suddenly when heated quickly to 85°, formaldehyde being evolved. The whole product was decomposed in this way, and the residue distilled under reduced pressure. A small fraction was collected, b. p. 115°/10 mm., which is the b. p. given by von Auwers (*loc. cit.*), but this was not homogeneous, had no methoxyl content, and consisted largely of benzaldehyde (recognised as the *o*-nitrophenylhydrazone). After the distillation, a considerable quantity of non-volatile semi-solid remained, which crystallised from a little methanol as white needles of 2 : 5-diphenyl-1 : 2 : 4-oxadiazole, m. p. and mixed m. p. with the authentic specimen, and with a specimen produced by the action of hydrochloric acid on the nitronic ester, 108°.

Ethyl Nitroacetate (XII).—This was prepared by a modification of the method of Bouveault and Wahl (*Bull. Soc. chim.*, 1904, **31**, 851) as follows. An ice-cold mixture of fuming nitric acid (60 g., *d* 1·5) and acetic anhydride (54 g.) was added dropwise to a mixture of ethyl acetoacetate (100 g.) and acetic anhydride (54 g.) at 30°. The temperature was kept between 30° and 35°, great care being taken not to exceed the upper limit. The mixture was added to ice-water (1000 c.c.) and stirred rapidly for 1 hour to remove nitric acid. The precipitated oil was then isolated by means of ether, mixed with an equal volume of absolute alcohol and boiled for 2 hours to decompose any remaining traces of acetic anhydride (failing this, the subsequent alkali extraction is rendered very inconvenient). The alcoholic solution was poured into water, extracted with ether, and the ether washed with dilute aqueous sodium carbonate until the alkaline layer was no longer yellow. The combined alkaline solutions were acidified; the precipitated oil, isolated by means of ether, distilled as a colourless oil, b. p. 89—91°/12 mm. (yield, 30%).

The ethereal solution, from which the nitro-ester had been extracted with alkali, was dried and distilled, yielding 10 g. of the substance described by Bouveault and Wahl (*loc. cit.*) as " Bis anhydro nitroacetate d'ethyle," b. p. 154°/13 mm. This substance is actually ethyl furoxandicarboxylate, as on shaking with concentrated aqueous ammonia, it yields a colourless solid, which after crystallisation from boiling water has the m. p. 223° attributed by Wieland to the diamide of furoxandicarboxylic acid (*Annalen*, 1909, **367**, 52). The formation of the furoxan derivative in this reaction is doubtless due to a decomposition of ethyl nitro-oximidoacetate

(cf. Bouveault and Wahl, *Bull. Soc. chim.*, 1907, **81**, 679; Wieland, *loc. cit.*) and not to a decomposition of dinitroacetic ester.

Ethyl nitroacetate is readily soluble in sodium carbonate solution. Its alcoholic solution is coloured by a drop of a dilute solution of bromine in methanol; after 1—2 minutes the colour disappears. Decoloration of further bromine occurs very slowly, and in chloroform solution the ester does not decolorise bromine at all. The alcoholic solution gives no reaction with ferric chloride, even on standing.

Nitronic Methyl Ester from Ethyl Nitroacetate.—Dry ethereal diazomethane (from 20 g. of nitrosomethylurea) was cautiously added to ethyl nitroacetate (10 g.), dissolved in anhydrous ether (40 c.c.). When the vigorous reaction was complete, the solution was kept for 2 hours, filtered, and concentrated under diminished pressure; attempts to distil the resulting oil were fruitless (see below). A fresh specimen of the nitronic ester was estimated for alkoxyl content after drying for 24 hours in a vacuum (Found : RO, 21·3. $C_5H_9O_4N$ requires 2RO, 21·8%). This nitronic ester should be handled with extreme care, as in contact with the skin it produces extremely persistent and painful blisters, which often take a long time to heal.

Decomposition of the Nitronic Ester.—(a) When heated quickly to 90°, the nitronic ester decomposes explosively with evolution of formaldehyde (detected). On attempted distillation, an explosion occurred at 0·1 mm. (bath temperature, 90°) and at 0·01 mm. the decomposition occurred at 65° (bath temperature). The products of this decomposition were distilled : (i) b. p. 98—105°/15 mm., (ii) b. p. 105—108°/15 mm., and (iii) 108—109°/15 mm. Fractions (ii) and (iii), when cooled and scratched, solidified and yielded *iso*nitrosoacetic ester, white crystals from ether–light petroleum, m. p. 30° (Found : EtO, 38·4. Calc. for $C_4H_7O_3N$: 1EtO, 38·4%).

(b) The nitronic ester (0·1180 g.) was added to cold colourless azeotropic hydriodic acid (4 c.c., freshly distilled) in an atmosphere of carbon dioxide. There was an immediate formation of iodine, and the mixture was agitated for 30 seconds, and then diluted with water (30 c.c.) and titrated with $N/10$-thiosulphate (Found : 1·93 atoms of iodine per molecule of ester).

(c) When the nitronic ester (10 g.) was treated with concentrated hydrochloric acid, the temperature rose almost to the boiling point; nitrous fumes were not evolved (cf. the action of hydrochloric acid on the nitronic methyl ester from methyl nitromalonate). The solution was diluted with water (50 c.c.), and the oil isolated by means of ether and eventually solidified and crystallised from chloroform and from light petroleum (b. p. 60—80°), forming long white needles, m. p. 80°, of chloro-oximinoacetic ester (Found : EtO, 30·3. Calc. for $C_4H_6O_3NCl$: 1EtO, 29·6%). The same result was obtained by the action of concentrated hydrochloric acid on the nitronic ester at — 10°, the temperature being allowed to rise to room temperature when the reaction was over. The chloro-oximinoacetic ester was identified by its reaction (Wieland, *Ber.*, 1907, **40**, 1675) : the cold aqueous solution of the ester was treated with dilute aqueous sodium carbonate; an oil then separated, which was identified as furoxandicarboxylic ester by its transformation into the diamide with concentrated aqueous ammonia, m. p. and mixed m. p. with the specimen obtained from the by-product of Bouveault and Wahl, 223°. The aqueous solution of chloro-oximinoacetic ester, on warming, also affords furoxandicarboxylic ester, a fact not mentioned by Wieland. It is stated in the literature (Beilstein) that chloro-oximino-acetic ester is transformed by water into oxalic acid and hydroxylamine hydrochloride.

(d) The nitronic ester was shaken with aqueous 2N-sodium hydroxide (2 vols.); heat was spontaneously developed and a yellow solution with an oil in suspension was produced. After neutralisation with hydrochloric acid, the mixture was shaken with concentrated aqueous ammonia; the oil then disappeared, but no solid separated. On cooling to — 10°, however, a white solid separated, which after crystallisation from water, softened at 119° and decomposed vigorously at 120—121° to a dark red-brown oil. This is the behaviour of the diamide of " bis anhydro nitroacetic acid " described by Scholl (*Ber.*, 1901, **34**, 868, 876), who obtained the ester, and other products, by the action of silver nitrite on bromoacetic ester. There is no doubt that this ester differs from furoxandicarboxylic ester, but the authors doubt the formula ascribed to the ester by Scholl. It is remarkable that the action of hydrochloric acid on the nitronic ester ultimately leads to furoxandicarboxylic ester, whereas the action of alkali gives its isomeride (Scholl). The latter compound has hitherto been obtained *only* by Scholl; all other references in the literature concerning " bis anhydro nitroacetic ester " refer to furoxandicarboxylic ester, and the references in Richter's " Lexicon " under $C_6H_{10}O_6N_2$ are to be corrected accordingly.

Methyl Nitromalonate (compare Franchimont and Klobbie, *Rec. trav. chim.*, 1889, **8**, 283; Willstätter and Hottenroth, *Ber.*, 1904, **37**, 1779; Wahl, *Bull. Soc. chim.*, 1901, **25**, 926).—The literature relating to the preparation of this compound is very unsatisfactory, and the following

Decomposition of the methylated product.   (a) When plunged into a bath at 90°, the compound decomposed suddenly, formaldehyde was evolved, and a dark tarry residue was obtained.   This should have contained *iso*nitrosoacetophenone, but since attempts to isolate this substance were fruitless, the residue was submitted to a degradative reaction of *iso*nitrosoacetophenone described by Claisen (*Ber.*, 1897, **20**, 656).   The tarry material was boiled for a few minutes with aqueous caustic soda ; a clear solution was then formed and on acidification benzoic acid and hydrocyanic acid were produced and recognised.

(b) On warming for 1 minute with concentrated hydrochloric acid the original ketone was produced, m. p. and mixed m. p. 106°.

(c) The partial regeneration of the starting material from the methylated product by the action of hydrochloric acid gave rise to the suspicion that the latter might be a mixture of the nitronic ester with some nitro-α-methoxy-α-phenylethylene, that is, the enol ether.   An attempt was therefore made to estimate roughly the amount of nitronic ester present, by assuming that two atoms of iodine per molecule of the nitronic ester are liberated when the mixture is treated with colourless azeotropic hydriodic acid.   This was carried out in the manner described under nitroacetic ester, and the result was the formation of 1·3 atoms of iodine per molecule of $C_9H_9O_3N$, which, on the above assumption, indicates a mixture of about 65% of nitronic ester and 35% of enol ether.

The methylation was repeated by adding the powdered ketone to a solution of diazomethane, but the results differed in no way from those already described.

2.   *The Alkaloids of* Ulex europaeus.   *Part I.*

By G. R. CLEMO and R. RAPER.

Ulex europaeus, the common gorse, was first examined for alkaloids by Gerrard (*Pharm. J.*, 1886, **17**, 109, 227 ; 1888, **19**, 1029 ; 1889, **20**, 1017), who obtained from the seeds, bark, and shoots a crystalline base to which he gave the name ulexine and the formula $C_{11}H_{14}ON_2$.   He stated that it differs from cytisine, but later workers (Partheil, *Ber.*, 1890, **23**, 3201 ; 1891, **24**, 634 ; van der Moer and Plugge, *Arch. Pharm.*, 1891, **229**, 48) asserted that the base from the seeds is cytisine.   More recently Klein and Farkas (*Oester. Bot. Zeit.*, 1930, **79**, 107) were unable to find cytisine in the plant.

During the past two seasons we have examined the young shoots.   Extracts of them in dilute hydrochloric acid were basified, and shaken with chloroform.   Evaporation of this left a brown resinous mass, from an alcoholic solution of which we obtained a picrate, m. p. 242°, whereas cytisine picrate we find to decompose at 270°.   The base recovered from this picrate was a lævorotatory resin, analysis of which, and of its picrate, picrolonate, platinichloride, and methiodide, suggested that it was anagyrine.   Messrs. T. and H. Smith of Edinburgh kindly placed at our disposal some alkaloidal extract of the seeds of *Anagyris foetida*, and we find that the picrates of anagyrine and of the base from *Ulex europaeus* melt at 242° alone or mixed.

The presence of anagyrine in the plant is seasonal, and it only occurs in the young shoots from their budding in May till the end of July in quantity sufficient to allow of extraction.   Our best yields (0·02% of the weight of shoots) were obtained in early June, decreasing to nil by the middle of August.   On one occasion we isolated a few milligrams of a crystalline base, $C_{15}H_{20}O_5N_2$.

The work on this and related plants is being continued.

EXPERIMENTAL.

Extraction of the Alkaloid.—Freshly gathered shoots (7500 g.) were finely minced and soaked for 24 hours in hydrochloric acid (1%).   After removal of plant debris in a filter-press the liquid

was mixed with 0·5% of its weight of Metasil A, passed through a Metafilter, basified (10N-sodium hydroxide), mixed with 1·5% of its weight of Metasil A, and again passed through the filter. The Metasil and slimy matter removed appeared to be free from the alkaloid. The clear brown filtrate was extracted five times with chloroform, on evaporation of which a brown, characteristically smelling resin was left. Addition of alcoholic picric acid to this precipitated a brown viscous mass, which soon became granular (4·2 g.) and on crystallisation from alcohol gave prisms, m. p. 242° (1·4 g.). The base recovered from this was a yellow varnish (0·6 g.), b. p. 195—200°/1 mm. (Found : C, 74·4, 73·5, 73·7; H, 8·6, 8·7, 8·7; N, 11·0, 11·8, 11·0. Calc. for $C_{15}H_{20}ON_2$: C, 73·7; H, 8·2; N, 11·5%). $[\alpha]_D^{20°}$ in chloroform − 148·5° (c = 0·75%). It gives a red colour with ferric chloride discharged by hydrogen peroxide, a brown amorphous precipitate with potassium tri-iodide, and a yellow precipitate with sulphur and hydrogen sulphide in ether.

The *picrate*, re-formed from the base, crystallises from alcohol in long prisms, m. p. 242° (Found : C, 53·6, 53·2, 53·5; H, 5·0, 5·6, 5·3; N, 14·1, 14·7, 14·7. $C_{15}H_{20}ON_2,C_6H_3O_7N_3$ requires C, 53·3; H, 4·9; N, 14·8%). The *picrolonate* forms brownish-red rosettes from alcohol, decomp. 254° (Found : C, 58·75, 58·9; H, 5·6, 5·25. $C_{15}H_{20}ON_2,C_{10}H_8O_5N_4$ requires C, 59·05; H, 5·5%). The platinichloride forms large orange-red prisms from hydrochloric acid (Found : C, 26·1, 26·6, 26·3; H, 3·8, 4·0, 3·85; N, 3·9; Pt, 28·0, 27·9, 28·4. Calc. for $C_{15}H_{20}ON_2,H_2PtCl_6,2H_2O$: C, 26·1; H, 3·8; N, 4·1; Pt, 28·3%). The methiodide, from the base and methyl iodide in warm acetone, forms square colourless plates from methyl alcohol, decomp. 264° (Found : C, 49·45; H, 5·7. Calc. for $C_{16}H_{23}ON_2I$: C, 49·7; H, 5·95%).

Anagyrine picrate, from authentic anagyrine ånd picric acid, forms yellow prisms indistinguishable under the microscope from the above picrate, m. p. 242° alone or mixed (Found : C, 53·2; H, 4·9%).

Cytisine picrate forms yellow prisms from alcohol, decomp. 270° (Found : C, 49·0; H, 4·2. $C_{11}H_{14}ON_2,C_6H_3O_7N_3$ requires C, 48·7; H, 4·05%).

On one occasion the solution from which the anagyrine had been extracted was acidified and evaporated to dryness in a vacuum, the residue basified (potassium carbonate) and extracted with ether, and the solvent removed ; a small residue was left which solidified and then formed lustrous plates from ligroin, m. p. 170° (Found : C, 58·3; H, 6·2; N, 9·0. $C_{15}H_{20}O_5N_2$ requires C, 58·4; H, 6·5; N, 9·1%).

Our thanks are due to Mr. O. Telfer for the microanalyses.

3. *Alkaloids of* Senecio. *Part I. Retrorsine.*

By G. BARGER, T. R. SESHADRI, H. E. WATT, and T. YABUTA.

THE genus *Senecio*, with 1250 species, is the largest of the *Compositae* and has provided more alkaloids than all the other genera combined. A number of its species are responsible for cattle poisoning, particularly in South Africa ; this led to the investigation by one of us (Watt, J., 1909, **95**, 466) of material considered at the time to be *S. latifolius* D.C., from which two alkaloids, senecifoline and senicifolidine, were isolated ; Cushny (*J. Pharm. Exp. Ther.*, 1911, **2**, 531) showed them to produce the liver degeneration characteristic of the intoxication. More recently botanists have divided *S. latifolius* into several species and the source of the above alkaloids is uncertain ; perhaps the botanical material was not homogeneous (see Steyn, " The Toxicology of Plants in S. Africa," Central News Agency Ltd., S. Africa, 1934 ; J. M. Watt and Breyer-Brandwyk, " The Medicinal and Poisonous Plants of Southern Africa," Edinburgh, 1932). Before this was realised we received a further supply of so-called *S. latifolius* which yielded neither of the two alkaloids previously isolated, but a third closely related base, which we have since also obtained from accurately identified *S. retrorsus* D.C. It is identical with the retrorsine of Manske (*Canadian J. Res.*, 1931, **5**, 651). Since other species have yielded still further alkaloids, to be described later,

and all are hydrolysed to closely related acids and bases, we consider Manske's nomenclature of " necines " and " necic acids " very suitable, *e.g.*,

$$C_{18}H_{25}O_6N + 2H_2O = C_8H_{13}O_2N + C_{10}H_{16}O_6$$

retrorsine   retronecine   retronecic acid
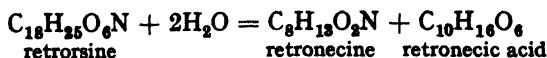
We established this equation some ten years ago and were at first at a loss to explain the discrepancy with the older results (H. E. W.). There is, however, also great similarity; indeed the hydrolytic product senecifolinine (J., 1909, **95**, 473) is perhaps identical with retronecine (see experimental part); its parent alkaloid is certainly different, and the other fission product, senecifolic acid, differs in melting point and rotation from retronecic acid, with which it is isomeric. Retronecine contains neither *O*-methyl nor *N*-methyl groups, does not react with nitrous acid, forms a quaternary iodide by the addition of methyl iodide, and is evidently a tertiary base; the nitrogen atom may belong to two rings (probably pyridine and pyrrolidine). The base contains two reactive hydrogen atoms (Zerewitinoff) and on boiling with acetic anhydride yields a diacetyl derivative. Manske obtained, at a lower temperature, only a monobenzoyl derivative and concluded, from the coloration formed with piperonal and alkali, that a $CH_2\cdot CO$ group is present. We have quite failed to demonstrate a ketone group in the molecule. It is conceivable that the group $CH_2\cdot CO$, if present, reacts in the enolic form with acetic anhydride. The diacetyl derivative is peculiar in losing one acetoxy-group on catalytic reduction, four hydrogen atoms being taken up; after hydrolysis the net result is the change from $C_8H_{13}O_2N$ to $C_8H_{15}ON$; the mechanism may be illustrated as follows :

$$
\begin{array}{ccccc}
\overset{|}{C}O & & \overset{|}{C}\cdot O\cdot CO\cdot CH_3 & & \overset{|}{C}H_2 \\
\overset{|}{C}H_2 & \xrightarrow{Ac_2O} & \overset{||}{C}H & \xrightarrow{2H_2} & \overset{|}{C}H_2 + CH_3\cdot CO\cdot OH \\
H\overset{|}{C}\cdot OH & & H\overset{|}{C}\cdot O\cdot CO\cdot CH_3 & & H\overset{|}{C}\cdot O\cdot CO\cdot CH_3
\end{array}
$$
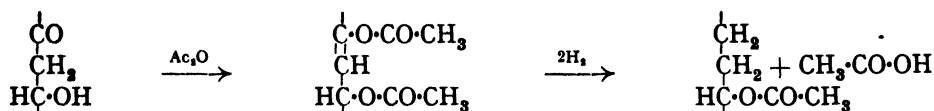
The base $C_8H_{15}ON$ is the monohydroxy-derivative of a hypothetical isomeride of tropane, $C_8H_{15}N$, which we propose to call retronecane (perhaps identical with piperolidine of Löffler and Kaim, *Ber.*, 1909, **42**, 96, and octahydropyrrocoline of Clemo and Ramage, J., 1932, 2970). Retronecine might then be retronecanolone; the base $C_8H_{15}ON$ can be called retronecanol, etc. We have compared the catalytic reduction of retrorsine, retronecine, and diacetylretronecine. With platinum oxide of Adams and Shriner, all three bases took up four hydrogen atoms rather rapidly; with palladium and hydrogen at two atmospheres the result was similar for the first and the third base (both acyl derivatives), but retronecine was reduced much more slowly, and after two hydrogen atoms had been taken up a substance resulted which was transformed by traces of mineral acid into an analogue of pyrrole-red. (A new " necine " to be reported on later, shows the same extreme sensitiveness to acids even before reduction.) On further reduction with palladium the stable retronecanol was obtained, which can be distilled with steam. On oxidation with chromic acid it yielded an amphoteric substance, which was esterified with ethyl alcohol; the ester was distilled and converted into a crystalline methiodide, $C_9H_{13}O_2NI$, which is therefore presumably derived from an acid $C_5H_4N\cdot CO_2H$ (picolinic?). We hope to identify it when more material is available.

Retronecic acid is a dihydroxydicarboxylic acid, $C_{10}H_{16}O_6$ (isomeric with dihydroxy-camphoric), and yields a lactone acid, $C_{10}H_{14}O_5$. Apart from this, our older experiments mostly yielded negative results; since then dehydrogenation by selenium has come into vogue and recent experiments indicate that this method furnishes a promising degradation of the acid. Retronecine and retronecic acid may be combined in retrorsine by two or by one ester linking; in the latter case the second molecule of water used up in hydrolysis would hydrolyse a lactone group. Retrorsine does not react with diazomethane, gives a *monophenylcarbamate*, and gives off two molecules of methane with the Grignard reagent. One of the active hydrogens must belong to a hydroxyl group in the acidic moiety; the other is either in the second hydroxyl or, if in a lactone group, there must be an active hydrogen in the basic moiety.

EXPERIMENTAL.

Retrorsine is readily soluble in alcohol and in chloroform, slightly in water, acetone, and ethyl acetate, hardly in ether. Water does not precipitate it from alcoholic solution, but when the alcohol is boiled off and the solution concentrated, it suddenly separates in leaflets. It is conveniently recrystallised from ethyl acetate or from 13 parts of boiling methyl ethyl ketone; m. p. 212° (Manske, 214—215° corr.) (Found : C, 61·6; H, 7·1. Calc. for $C_{18}H_{25}O_6N$: C, 61·5; H, 7·1%). In ethyl alcohol ($l = 1, c = 1·99$), $\alpha_D^{18°} - 0·35°$, $[\alpha]_D^{18°} - 17·6°$.

0·1613 G. in anisole, treated at 120—125° for 15 minutes with excess of methylmagnesium iodide, gave 23·0 c.c. of methane (equiv. to 2·2 reactive hydrogen atoms). Nitrous acid and diazomethane were without action.

Retrorsine Monophenylcarbamate.—The alkaloid (0·5 g.) and phenyl *iso*cyanate (1·5 c.c.) were boiled in chloroform (10 c.c.) for 2 hours, and the solvent and excess of the reagent then removed in a vacuum at 100°. The brown viscous residue was washed with cold benzene and extracted with warm dilute hydrochloric acid. The *carbamate*, precipitated by ammonia, was extracted with ether; it separated from the dried and concentrated solution as prismatic needles, m. p. 200—202° (Found : C, 64·2; H, 6·5; N, 6·2. $C_{25}H_{30}O_7N_2$ requires C, 63·8; H, 6·4; N, 6·0%).

Retrorsine nitrate, prepared by addition of nitric acid to a concentrated solution of the alkaloid in absolute alcohol and recrystallised from alcohol–ether, formed prisms, m. p. 145° (Found : loss in a vacuum at 100°, 5·4. $C_{18}H_{25}O_6N,HNO_3,\frac{1}{2}C_2H_5\cdot OH$ requires $C_2H_5\cdot OH$, 5·3%).

Retrorsine methiodide crystallised from 50% methyl alcohol in prisms, m. p. 260° (Manske, 266° corr.), readily soluble in water, sparingly in alcohol (Found : C, 45·9; H, 5·6; I, 25·7. Calc. for $C_{19}H_{28}O_6NI$: C, 46·2; H, 5·7; I, 25·8%).

Retrorsine Perbromide.—When a 2% solution of bromine was dropped into one of the base, in chloroform, four atomic proportions were used up and orange-yellow prisms separated, which were recrystallised from methyl alcohol (Found : Br, 41·2. $C_{18}H_{25}O_6NBr_2,HBr$ requires Br, 40·5%). On treatment with sulphurous acid retrorsine was recovered. The hydrogen bromide doubtless results from partial conversion into a bromo-derivative remaining in the mother-liquor.

Hydrolysis of Retrorsine.—The alkaloid is slowly hydrolysed by boiling concentrated hydrochloric acid; with *N*-sodium hydroxide, 2 hours' boiling suffices. Owing to the solubility relations of the fission products, the following process is very suitable. The alkaline solution is made acid to Congo-red, evaporated almost to dryness, mixed with plaster of Paris, and exhaustively extracted with dry ether (Soxhlet; about 30 hours). Retronecic acid crystallises from the boiling ether in the receiver. When alcoholic sodium hydroxide is used (as Watt did for senecifoline), the ethereal mother-liquor leaves a syrup (ester ?), from which more acid can be recovered after a second hydrolysis. After extraction with ether, the plaster of Paris is freed from ether by exposure to the air, well ground with anhydrous sodium carbonate (20 g. for 10 g. of alkaloid), returned to the Soxhlet apparatus, and extracted with chloroform (16 hours). The oily residue of retronecine, left on evaporation, crystallises in a vacuous desiccator. It is recrystallised from acetone, forming stout prisms which may be an inch long. With half the above quantity of sodium carbonate a fraction very sparingly soluble in acetone is obtained and identified as the hydrochloride. The yield of retronecine and of retronecic acid is almost quantitative.

Retronecine, m. p. 121—122° (Found : C, 61·5; H, 8·3. Calc. for $C_8H_{13}O_2N$: C, 61·9; H, 8·4%), shows in ethyl alcohol ($l = 1, c = 1·83$) $\alpha_D + 0·93°$, $[\alpha]_D + 50·2°$. 0·07179 G. in anisole gave with methylmagnesium iodide 20·6 c.c. of methane (equiv. to 2·0 reactive hydrogen atoms). Retronecine is very readily soluble in water and in alcohol, moderately in acetone and in chloroform, slightly in ether. An aqueous solution, strongly alkaline to litmus, does not yield a precipitate with picric acid, potassium mercuric iodide, or potassium bismuth iodide, but does with phosphotungstic acid. On distillation with zinc dust the vapours give the pyrrole reaction on pinewood. There is no reaction with nitrous acid. The Schotten–Baumann reaction gives a neutral, and phenyl *iso*cyanate a basic, product; both are soluble in ether, and neither could be crystallised. No *p*-nitrophenylhydrazone could be obtained, and no phenylosazone; Fehling's solution is not reduced. No benzylidene compound could be isolated, whether alcoholic sodium hydroxide or hydrogen chloride was used as condensing agent; there merely resulted a dark solution, as reported by Manske.

Retronecine hydrochloride forms prisms from absolute alcohol, m. p. 161° (Manske, 164°

corr.) (Found : C, 49·9; H, 7·2. Calc. for $C_8H_{12}O_2N,HCl$: C, 50·1; H, 7·3%). In ethyl alcohol ($l = 1$, $c = 1·50$) $\alpha_D^{15°} - 0·24°$, $[\alpha]_D^{15°} - 16°$ (another preparation and another observer : m. p. 162—163°, $[\alpha]_D^{15°} - 13·7°$). Watt gives for senecifolinine hydrochloride, m. p. 168°, $[\alpha]_D^{20°} - 12·6°$. His analysis, calculated for $C_8H_{11}O_2N,HCl$, agrees better with $C_8H_{12}O_2N,HCl$. His aurichloride had m. p. 150°; we found for retrorsine aurichloride, m. p. 146°. The two bases are evidently very similar, but identity cannot be established without a direct comparison.

Diacetylretronecine.—When retronecine was boiled with acetic anhydride for $\frac{1}{4}$ hour, the solution darkened and became fluorescent. After removal of the excess of acetic anhydride in a vacuum, distillation with water, and addition of aqueous picric acid, a *picrate* rapidly crystallised (yield, 80%), which formed prisms from water, m. p. 146° (Found : C, 46·1; H, 4·4. $C_{18}H_{20}O_{11}N_4$ requires C, 46·2; H, 4·3%).

On evaporation of its aqueous solution, the acetate of the free base remained as a syrup, which was mixed with plaster of Paris and sodium carbonate; after continuous extraction with chloroform the liquid residue distilled at 125° in a high vacuum; the distillate showed a strong green fluorescence, but nevertheless gave the same picrate. It readily reacted with methyl iodide; the *methiodide* was crystallised from alcohol–ether, m. p. 118—120° (Found : I, 33·0. $C_{13}H_{20}O_4NI$ requires I, 33·3%).

Reduction of Retronecine.—Boiling for several hours with zinc dust and acetic acid, or in alcoholic solution with the addition of 12 atomic proportions of sodium, had no effect; after mixing with plaster of Paris and extraction with chloroform, unchanged retronecine was recovered almost quantitatively. Reduction in 33% acetic acid, with palladium and hydrogen under 2 atmospheres, proceeded slowly and gave, after absorption of 1 mol. of hydrogen, a slightly coloured syrup with an odour of acetamide, transformed by traces of mineral acids into an insoluble red resin. With platinum oxide (according to Willstätter and Waldschmidt-Leitz, later according to Adams and Shriner) two molecules of hydrogen were rapidly taken up and the product yielded a picrate of retronecanol, m. p. 208° (see below).

Reduction of Retrorsine.—This starts rapidly in dilute acetic or alcoholic solution, both with palladium and with platinum oxide; ultimately some 6 hours may be required under atmospheric pressure. Two molecules of hydrogen are taken up. The reduced alkaloid is very soluble in chloroform, and is precipitated by ether as a white amorphous powder. It is extremely soluble in water, much more than the parent alkaloid, and could not be crystallised. It did not react with diazomethane nor could a free carboxyl group be demonstrated by esterification with alcohol and hydrogen chloride. In contradistinction to retrorsine, the hydrogenated alkaloid is precipitated by aqueous picric acid, but neither the picrate nor the methiodide could be obtained pure. On hydrolysis, as described for retrorsine, unchanged retronecic acid was obtained, together with a new base, retronecanol, which was volatile with steam. The distillate was acidified and evaporated. After grinding with dry potassium carbonate, the residue was extracted with ether; the syrupy base so obtained gave the same *picrate*, m. p. 208°, as that mentioned above. It formed prisms from water and from alcohol (Found : C, 45·7, 45·8; H, 4·8, 4·8. $C_8H_{15}ON,C_6H_3O_7N_3$ requires C, 45·5; H, 4·9%).

Acetylretronecanol.—Reduction of diacetylretronecine, like that of retrorsine, proceeds with palladium more readily than the reduction of retronecine itself. The product was isolated as *picrate*, m. p. 176°, which crystallised from 95% alcohol in long prisms (Found : C, 46·6; H, 4·8; N, 13·6. $C_{10}H_{17}O_2N,C_6H_3O_7N_3$ requires C, 46·6; H, 4·9; N, 13·6%). The same picrate was obtained by acetylating retronecanol (above). Acetylretronecanol, regenerated from this picrate, was slowly extracted from alkaline aqueous solution by chloroform. After drying, it distilled at 107°/12 mm. but did not crystallise in the ice chest. The oily base reacts violently with methyl iodide, with considerable decomposition; it should be diluted. The *methiodide* formed stout prisms from alcohol, m. p. 207—208° (Found : C, 41·0; H, 6·1; I, 40·3. $C_{11}H_{20}O_2NI$ requires C, 40·6; H, 6·2; I, 39·1%).

Oxidation of Retronecanol.—The base (1 g.) was dissolved in water (4 c.c.) and sulphuric acid (0·4 g.), and heated with a mixture of chromic acid (1 g.), sulphuric acid (1·4 g.), and water (20 g.). After 1 hour an equal quantity and after another hour half the quantity of chromic acid were added, making in all 5 oxygen atom equivalents. After 4 hours, when no more chromic acid was being used up, the excess was reduced by sulphur dioxide. The solution was nearly neutralised with barium hydroxide, and the precipitate boiled with water. The remaining sulphuric acid was removed from the combined filtrates by barium carbonate. The neutral solution, containing a soluble sulphate, was evaporated, and the residue extracted with alcohol. After repeated esterification with hydrogen chloride, the ester was liberated with potassium carbonate, extracted by ether, and distilled at about 140°/10 mm. The pale brown distillate

did not yield a crystalline picrate, but in acetone solution a colourless *methiodide* was formed, which crystallised from alcohol in rhombohedral plates, m. p. 292—295° (Found : C, 36·9; H, 4·2; I, 43·3. $C_9H_{12}O_2NI$ requires C, 36·9; H, 4·1; I, 43·3%).

Retronecic Acid.—This acid is best crystallised from a little boiling water, or from ethyl acetate; it forms narrow prisms, m. p. 177° (Found : C, 51·7; H, 6·9; equiv., by titration, 117. Calc. for $C_{10}H_{16}O_5$: C, 51·7; H, 6·9%; equiv., 116). In ethyl alcohol ($l = 1, c = 1·32$), $\alpha_D - 0·15°$, $[\alpha]_D - 11·36°$. The acid is not oxidised by ammoniacal silver nitrate, or reduced catalytically by hydrogen, nor does it decolorise bromine water. A lactone group is absent (back titration). The silver salt crystallises in needles from hot water. The methyl ester is syrupy and distils at about 200° in a high vacuum. Boiling concentrated hydrobromic acid did not attack the acid, but at 150—160° in a sealed tube it charred it completely. When retronecic acid was heated with anhydrous oxalic acid for some hours at 120—130°, formic acid was given off. The reaction mixture was freed from oxalic acid by boiling with calcium carbonate; on concentration the calcium salt of another acid crystallised. After acidification, mixing with plaster of Paris, and extraction with ether, this acid was obtained in plates, m. p. 181—183°; it is doubtless identical with Manske's lactone acid, m. p. 186° (corr.) [Found : C, 56·1; H, 6·6; equiv., by direct titration, 217; by back titration (a) in the cold, 205, (b) after boiling with sodium hydroxide, 104. Calc. for $C_{10}H_{14}O_5$: C, 56·1; H, 6·5%; equiv., as monobasic acid, 214].

4. *The Inversion of α-Substituted Hydroxyhydrindeneacetic Acids.*

By D. H. PEACOCK and B. K. MENON.

IT has been shown (J., 1934, 1296) that lactones of type (I) undergo inversion at the α-carbon atom when R = CH_2Ph but not when R = Me or *n*-Bu and it was suggested that the difference is due to the electron affinity of the benzyl group. We have now found that inversion takes place when R = $CH_2·CH_2Ph$ or $CH_2·C_6H_4Br$ (*p*), thus confirming the suggestion that the phenyl group aids inversion and supporting the hypothesis that it is the electron affinity of the phenyl group which assists the process. The *lactone* (I*a*; R = $CH_2·CH_2Ph$) was readily formed from the corresponding *acid*, and inversion took place much more slowly than when R = CH_2Ph, as would be expected; there was also an indication that the equilibrium mixture contained the two forms in comparable amounts. When R = CH_2Ph, the equilibrium mixture contained almost exclusively the *b* form of the lactone. The substitution of $CH_2·CH_2Ph$ for CH_2Ph seems, therefore, to affect not only the speed of inversion but also the position of equilibrium in the mixture formed.
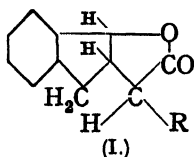
trans-γ-Phenyl-α-1-hydroxyhydrindene-2-butyric Acid.—Ethyl β-phenylethylacetoacetate (23·4 g.; Auwers and Moller, *J. pr. Chem.*, 1925, 109, 124) and solutions of sodium (2·3 g. in 50 c.c.) and of 2-bromo-1-hydroxyhydrindene (21·3 g. in 50 c.c.) in absolute alcohol were mixed and boiled for 2 hours. The product of hydrolysis by alcoholic caustic potash, liberated by acidification, was a thick oil, which partly crystallised on addition of benzene. The *acid* was recrystallised from benzene (yield, 4 g.); m. p. 131° (Found : C, 76·7; H, 6·95. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%).

cis-Lactone (I*a*; R = $CH_2·CH_2Ph$).—The preceding acid (4 g.) was boiled for 2 hours with an acetic acid solution of hydrogen bromide (20 c.c.). The acetic acid and hydrogen bromide were then distilled under reduced pressure and the *lactone* was dissolved in benzene, shaken with sodium bicarbonate solution, dried, recovered, and crystallised from benzene; m. p. 94° (yield, 2·65 g.) (Found : C, 81·6; H, 6·6. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%).

cis-Lactone (I*b*; R = $CH_2·CH_2Ph$).—The lactone (I*a*) (0·5 g.) was boiled with 25 c.c. of alcoholic *N*-sodium hydroxide : after ¼ hour the original lactone (m. p. 94°) was recovered, but

after 5 hours an oil was obtained which solidified when scratched and then crystallised (m. p. 73—74°) slowly from light petroleum.   When heated in a sealed tube for 2 hours at 150°, the same quantities of lactone and alkali gave a product, m. p. 72—74°, which, crystallised from light petroleum, gave a *lactone*, m. p. 88° (0·19 g.), and a mixture of lactones, m. p. 73—74° (0·18 g.). Similar products were obtained when the original lactone (0·5 g.) was heated with caustic potash (1 g. in 5 c.c. of water) for 3 hours at 130° (Found for the lactone, m. p. 88° : C, 81·5; H, 6·5; M, 274·5. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%; M, 278. Found for the lactone mixture, m. p. 73—74° : C, 80·6, 80·4, 80·6; H, 6·9, 6·75, 6·5%; M, 273·6. Consistently low results for carbon were obtained with this substance).

trans-β-p-*Bromophenyl-α-1-hydroxyhydrindene-2-propionic   Acid.*—Ethyl   *p*-bromobenzyl-acetoacetate (b. p. 218—220°/40 mm.; 30 g.), sodium (2·3 g.), and absolute alcohol (50 c.c.) were mixed and to the cold solution 2-bromo-1-hydroxyhydrindene (21·3 g.) in absolute alcohol (50 c.c.) was added.   Next day the mixture was boiled for 2 hours and was then neutral.   The crude acid (10 g.), on crystallisation from benzene, gave the desired *acid*, m. p. 175° (Found : Br, 21·95. $C_{18}H_{17}O_3Br$ requires Br, 22·2%), and a mixture of this acid with β-*p*-bromophenylpropionic acid. This mixture on treatment with phosphorus pentachloride gave a product which after treatment with water yielded the *cis*-lactone described below and β-*p*-bromophenylpropionic acid.

cis-*Lactone* (Ia; R = *p*-$C_6H_4Br\cdot CH_2$).—The preceding acid (2 g.) was heated on a water-bath for 2 hours with a saturated solution of hydrogen bromide in acetic acid (20 c.c.) The *lactone* obtained, m. p. 134°, was soluble in ethyl alcohol and benzene–light petroleum (Found : Br, 23·5. $C_{18}H_{15}O_2Br$ requires Br, 23·3%).   The same lactone was obtained by the action of phosphorus pentachloride on a chloroform solution of the acid.

cis-*Lactone* (Ib; R = *p*-$C_6H_4Br\cdot CH_2$).—The above lactone (0·5 g.) was heated on a water-bath for 2 hours with alcoholic caustic potash (1 g. in 5 c.c.).   The neutral product was crystallised from alcohol; m. p. 110° (Found : Br, 23·1. $C_{18}H_{15}O_2Br$ requires Br, 23·3%).   A mixture of the two lactones melted at 122°.

Acetoxy-acid.—*trans*-β-*p*-Bromophenyl-α-1-hydroxyhydrindene-2-propionic acid (1 g.) was heated under reflux with acetic anhydride (5 c.c.) at 150—160° for 3 hours, and the acetic anhydride then distilled off.   The residue, washed with benzene and dilute sodium bicarbonate solution, had m. p. 252°; it was dissolved in aqueous alcohol, and added to sodium bicarbonate solution. On acidification the *acetoxy*-acid (0·9 g.) was obtained, m. p. 171° after crystallisation from benzene (Found : Br, 20·0. $C_{20}H_{19}O_4Br$ requires Br, 19·85%); mixed with the original acid, it melted at 152°.

No isomeric acetoxy-acid was obtained from the mother-liquor of the original acid.

5.   *The Benzylation of Amines. Part IV. The Rate of Reaction of Benzyl Bromide with Nitrobenzylaniline and some Derivatives.*

By D. H. PEACOCK.

THE rates of reaction of *m*-nitrobenzyl chloride with primary and with tertiary aromatic amines have been found to be faster than the rates for the *p*-compound (J., 1924, **125**, 1975; 1925, **127**, 2177; *J. Physical Chem.*, 1926, **30**, 673; 1927, **31**, 535; Baker, J., 1933, 1128, has confirmed these results for aniline); moreover, the energies of activation for the *m*- are smaller than those for the *p*-compound.   In the nitrobenzyl chlorides the halogen atom is separated from the nucleus by the methylene group, but when this atom is directly attached to the nucleus the order of reactivity of the *m*- and *p*-compounds is inverted (see Nagornoff, *A*., 1899, **76**, i, 425).   Experiments have therefore been carried out to determine whether a similar relationship holds for the nitroanilines and the nitrobenzylanilines.

It has already been shown (J., 1925, **127**, 2179; where the value of $k_{45°}$ for *p*-nitroaniline should read < 0·0002 instead of > 0·0002) that benzyl chloride reacts more rapidly with *m*- than with *p*-nitroaniline in methyl-alcoholic solution, and benzyl bromide has now been found to behave similarly in acetone solution (see table, p. 17).   If it be assumed that,

independently of theories of its mode of action and of the nature of X, the nitro-group will act consistently in compounds of the types (I) and (II), then, if the order is inverted in this

(I.) $NO_2\langle\rangle X$ $NO_2\langle\rangle CH_2 \cdot X$ (II.)

O_2N

(III.) $NO_2\langle\rangle CH_2 \cdot NH \cdot C_6H_4R$ $\langle\rangle CH_2 \cdot NH \cdot C_6H_4R$ (IV.)
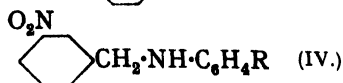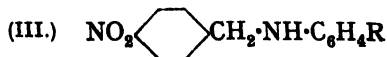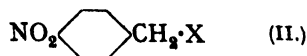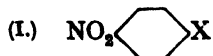
case also, benzyl bromide should react more rapidly with *p*- (III, R = H) than with *m*-nitrobenzylaniline (IV, R = H).

The matter can, however, be approached in another way. If the lower reactivity of *p*- than of *m*-nitrobenzyl chloride be ascribed to the greater electron-attractive effect of the nitro-group in the para-position, then (IV, R = H) should be more reactive than (III, R = H), since addition to the basic nitrogen atom would be expected to be helped by greater electron availability. Actually (see table, below) this was found to be the case. (One would expect the former to be a stronger base than the latter, but no data are available.) On the other hand, *p*-chloro-*p'*-nitrobenzylaniline (III, R = *p*-Cl) reacted more rapidly than its *m'*-isomeride (IV, R = *p*-Cl) with benzyl bromide. The effect of the nitrobenzyl group thus depends upon the nature of the base to which it is attached.

The results obtained with *p'*-nitrobenzyl-*p*-toluidine (III, R = *p*-Me) varied too greatly—possibly owing to separation of the solid hydrobromide during the reaction—for a comparison to be made with its *m'*-isomeride, but one unexpected result was definite, *viz.*, that the derivatives of *p*-toluidine reacted much more slowly than the corresponding derivatives of aniline. This seems the only known case in which the introduction of the methyl group in the para-position lowers the reactivity of an aromatic base towards a halogen compound; in all other cases the opposite result has been observed (see, *e.g.*, Menschutkin, *Z. physikal. Chem.*, 1900, **34**, 157; Thomas, J., 1913, **103**, 594; Peacock, *loc. cit.*; van Opstall, *Rec. trav. chim.*, 1933, **52**, 901).

The first and most obvious explanation of this behaviour is that amine reactivity in this case is determined by the ease of removal of the hydrogen atom rather than by electron availability at the nitrogen atom. This possibility was considered earlier (*J. Physical Chem.*, 1927, **31**, 535) and is the reason why tertiary as well as primary and secondary bases have been examined; but if this explanation were true, then the *m*-methyl group should lower the reactivity to a smaller extent than the *p*-, and the introduction of the chlorine atom should raise the reactivity of the compound above that of the unsubstituted compound. It was, however, found that *m'*-nitrobenzyl-*m*-toluidine (IV, R = *m*-Me) reacted more slowly than the *p*-toluidine derivative (IV, R = *p*-Me), and that the nitrobenzylchloroanilines reacted more slowly than the nitrobenzylanilines. Thus the nitrobenzyltoluidines resembled the toluidines. The chlorine atom behaved similarly to the methyl group in that the *p*-compound reacted faster than the *m*-. From these effects, the factor influencing reactivity seems to be electron availability at the nitrogen atom, and not the ease of elimination of a proton.

The results obtained are tabulated below; the solvent used was acetone.

Reaction of benzyl bromide with nitroanilines.

Base.	$10^3k_{35°}$.	$10^3k_{45°}$.	E, cals.
Meta	3·7	7·45	13,570
Para	0·36	0·73	13,600

Reaction of benzyl bromide with nitrobenzylaniline derivatives.

m-Nitrobenzyl derivative of	Temp.	10^3k.	*p*-Nitrobenzyl derivative of	Temp.	10^3k.
Aniline	˙35°	9·9	Aniline	35°	7·0
,,	45	17·2	,,	45	14·0
p-Toluidine	,,	1·7	*p*-Toluidine	,,	1—2
m-Toluidine	,,	1·17			
p-Chloroaniline	,,	0·18	*p*-Chloroaniline	,,	0·28
m-Chloroaniline	,,	0·14			

O

As regards the effect of the chlorine atom, the results are similar to those obtained in other experiments (unpublished) on *m-* and *p-*chloro- and -bromo-aniline; the halogenated anilines react more slowly than does aniline, and the *p-*substituted more rapidly than the *m-*substituted bases. These results are easily explicable on the assumption that the reactivity varies with the degree of electron availability or mobility at the nitrogen atom. The more readily these electrons are displaced to the positions corresponding to the activated state, the more readily the base reacts. The *p-* is more effective than the *m-*halogen atom in producing electron availability at the amino-group, and so the experimental results agree with those expected. *m-* and *p-*Chloro-*m'*-nitrobenzylanilines (IV, R = *m-* or *p-*Cl) behave similarly, and it may be concluded that here also reactivity increases with increased electron mobility at the nitrogen atom.

In these experiments the methylene group seems able to transmit an alternating effect to the nitrogen atom. Oxford and Robinson (J., 1926, 383) found that no alternating effect was transmitted to the benzene nucleus in the nitration of the *m-* and *p-*nitrobenzyl-oxyanisoles. If, therefore, an alternating effect reached the oxygen atom, it was not further transmitted to the benzene nucleus.

EXPERIMENTAL.

The velocity determinations were carried out as described in earlier papers. The bases used were all prepared as in the following typical case.

3-*Chloro-4'-nitrobenzylaniline.*—*p-*Nitrobenzyl chloride (17·2 g.) was mixed with *m-*chloroaniline (25 g.), sodium carbonate (5·3 g.), and water (50 c.c.), and stirred for 8—10 hours in a boiling water-bath. The product was steam-distilled to remove primary base, washed with dilute hydrochloric acid and then with aqueous sodium hydroxide, and crystallised from ethyl alcohol–ethyl acetate; m. p. 66°. The *substance* was dimorphous, separating in orange and in pale yellow crystals (Found : N, 11·1. $C_{13}H_{11}O_2N_2Cl$ requires N, 10·6%).

4-Chloro-3'-nitrobenzylaniline, m. p. 81° (from butyl alcohol). 4-*Chloro-4'-nitrobenzylaniline*, m. p. 99·5° (from ethyl alcohol) (Found : Cl, 13·1. $C_{13}H_{11}O_2N_2Cl$ requires Cl, 13·5%). 3-Chloro-3'-nitrobenzylaniline, m. p. 88°, and 3'-nitrobenzyl-*p*-toluidine, m. p. 89° (both from ethyl alcohol and ethyl acetate). 4'-Nitrobenzylaniline, m. p. 70·5° (Strakosch, *Ber.*, 1873, **6**, 1062, gives m. p. 68°; Paal and Sprenzer, m. p. 72°). *m-*Nitrobenzylaniline, m. p. 84—85° (Purgotti and Monti, *Gazzetta*, 1900, **30**, ii, 256, give m. p. 84·5°). 4'-Nitrobenzyl-*p*-toluidine, m. p. 68—69° (Lellmann and Meyer, *Ber.*, 1892, **25**, 3582), and 3'-nitrobenzyl-*m*-toluidine, m. p. 79·5° (Purgotti and Monti, *loc. cit.*, give 67°).

The velocity determinations were carried out in acetone, many of the bases used being sparingly soluble in methyl and ethyl alcohol. Other bases are being examined.

I thank the University of Rangoon for a grant.

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6. *The Properties of Some Optically Active Sulphonylthioethanes.*

By F. BARRY KIPPING.

IT has already been shown (J., 1933, 1507) that, when the optically active acid, α-*p*-carboxyphenylsulphonyl-α-*p*-tolylthioethane (IX),* is oxidised, an optically inactive disulphone (X) results :

(IX.) $CO_2H \cdot C_6H_4 \cdot SO_2 \cdot CHMe \cdot S \cdot C_7H_7 \longrightarrow CO_2H \cdot C_6H_4 \cdot SO_2 \cdot CHMe \cdot SO_2 \cdot C_7H_7$ (X.)

The active acid is also racemised by alkali and it seemed of interest to prepare another compound of the same type. dl-α-p-*Carboxyphenylsulphonyl-α-phenylthioethane* (XII) was therefore prepared from α-*p*-carbethoxyphenylsulphonylethyl methyl ketone (VIII) and diphenyl disulphoxide in a similar manner to the corresponding *p*-tolyl compound (IX, p. 1509) :

(VIII.) $CO_2Et \cdot C_6H_4 \cdot SO_2 \cdot CHMe \cdot COMe \longrightarrow CO_2H \cdot C_6H_4 \cdot SO_2 \cdot CHMe \cdot S \cdot C_6H_5$ (XII.)
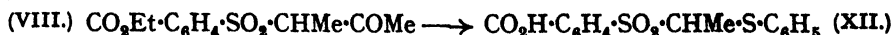
* Roman numerals I—XI refer also to J., 1933, 1506—1510.

As in the case of the *p*-tolyl compound, this acid was readily resolved into its optically active components, the *d*-acid being obtained by the crystallisation of the quinine salt, and the *l*-isomeride with the aid of *l*-menthylamine. The active acid was optically stable in chloroform and in acetic acid solutions; when it was dissolved in aqueous alcohol, sodium hydroxide in quantities up to 1 equiv. could be added without causing any racemisation, but amounts above this produced racemisation with a velocity which increased with the quantity of alkali added. When α-*p*-carboxyphenylsulphonyl-α-*p*-tolylthioethane was reinvestigated (*loc. cit.*, p. 1509), similar results were obtained with this acid.

More remarkable still was the racemisation of the methyl esters of (IX) and (XII) by small quantities of sodium methoxide.

These racemisations can only be explained by assuming the formation of a sodium salt from the esters, or from the normal sodium salt of the acid, with excess of alkali, by the displacement of the tertiary hydrogen atom attached to the α-ethane carbon atom. The formation of a salt, –S·CMe:SO(ONa)–, would naturally cause complete racemisation and this might also occur if the salt has the structure –S·CMeNa·SO₂–, the acidic ion being too unstable to retain its tetrahedral configuration. Efforts to isolate a sodium salt of the ester were, however, unsuccessful: when the ester of (XII) was treated with sodium methoxide (1 equiv.) in methyl-alcoholic solution, ether added, and the solution kept overnight, a precipitate separated. This proved to be the normal sodium salt of the acid, hydrolysis of the ester having taken place.

Oxidation of the active acid (XII) and its ester gave an optically inactive disulphone as with the acid (IX).

In order to show still more conclusively that the racemisation of these acids and their esters is due to the presence of a hydrogen atom attached to the α-ethane carbon atom, an acid lacking such a (mobile) hydrogen atom has been prepared. The ethyl ester of (X) was treated with sodium ethoxide and diphenyl disulphoxide in alcoholic solution and the *ethyl* ester of (XIII) was easily isolated; when this was hydrolysed in the usual way with excess of alkali, however, the phenylthio-group was eliminated, presumably as phenylsulphenic acid, and the acid (X) regenerated. On the other hand, by careful hydrolysis with one equivalent of aqueous-alcoholic alkali, the ester yielded dl-α-p-*carboxyphenylsulphonyl-α-p-tolylsulphonyl-α-phenylthioethane* (XIII),$CO_2H·C_6H_4·SO_2·CMe(SPh)·SO_2·C_7H_7$. This acid was again easily resolved into its optical antimerides, brucine giving the salt of the *l*-isomeride as the more sparingly soluble component, and *l*-menthylamine the salt of the *d*-acid.

As was expected, this acid was optically stable when dissolved in excess of one equivalent of alkali, and was recovered from its sodium salt unchanged in rotatory power : the active esters could not be conveniently examined in alcoholic solution with sodium ethoxide, as they are not sufficiently soluble in that solvent. Careful hydrolysis of the active esters with boiling aqueous-alcoholic alkali, however, gave an active acid of maximum rotation and it is therefore reasonable to suppose that the esters are stable towards sodium ethoxide.

Attempts to oxidise this acid and its esters to the corresponding trisulphone were unsuccessful.

<div align="center">EXPERIMENTAL.</div>

dl-α-p-*Carboxyphenylsulphonyl-α-phenylthioethane* (XII) crystallised from acetic acid in prisms, m. p. 167—168° (Found : C, 55·6; H, 4·5. $C_{15}H_{14}O_4S_2$ requires C, 55·8; H, 4·35%). The methyl ester, prepared by the hydrogen chloride method, crystallised from methyl alcohol in prisms, m. p. 72°. No sodium salt of this ester could be obtained. The ester was dissolved in methyl alcohol containing sodium methoxide (1 equiv.), and ether was added : on standing over-night, the sodium salt of the acid was isolated.

Resolution of dl-α-p-*Carboxyphenylsulphonyl-α-phenylthioethane.*—The *quinine* salt of the acid was first obtained crystalline from a mixture of absolute alcohol and petroleum (b. p. 60—80°) and was afterwards fractionated from alcohol, from which it separated in needles. The acid (33 g.) and quinine (33 g.) in alcohol (200 c.c.) deposited 40 g. of the quinine salt, m. p. 122—126°. $[\alpha]_{5461}$ —128° in chloroform ($c = 1$). After six crystallisations from alcohol, 20 g. of product were obtained, m. p. 136—138°. $[\alpha]_{5461}$ —97° in chloroform ($c = 1·06$). These values were unchanged by further crystallisation and refer to specimens dried at 80° in a vacuum

[Found : H_2O, 2·4, 2·9. $C_{15}H_{14}O_4S_2,C_{20}H_{24}O_2N_2,H_2O$ requires H_2O, 2·7%. Found : N (after drying at 80°), 4·4. Required, 4·3%]. The *d*-acid was obtained from the final fraction by dissolving the salt in acetic acid and adding water. It had m. p. 164—165° (Found : C, 56·0; H, 4·7%), $[\alpha]_{5780} + 113°$, $[\alpha]_{5461} + 134°$ in chloroform ($c = 0·75$).

The acid recovered from the initial mother-liquors was dissolved in alcohol, and 1 equiv. of *l*-menthylamine hydrochloride and sodium hydroxide added successively. A menthylamine salt was precipitated which, after crystallisation from alcohol, was finally obtained in fine needles, m. p. 182—183°, $[\alpha]_{5461} - 95°$ in chloroform ($c = 0·5$). The acid from this had $[\alpha]_{5461} - 134°$ in chloroform.

The following weights of acid were dissolved in 5 c.c. of alcohol, the specified quantity of sodium hydroxide ($N/10$-solution) added, and the solution made up to 20 c.c. with water and examined at once in a 2 dcm. polarimeter tube. The values of $[\alpha]$ are calculated on the weight of acid taken.

Wt. of acid, g.	Equivs. of sodium hydroxide.	$[\alpha]_{5461}$.	Approximate time from addition of alkali.
0·1177	0·99	+123°	2 mins. and 12 hrs.
0·1032	0·997	+120	,, ,, ,,
0·1612	1·035	+100	1·5 mins.
		+ 80	13 mins.
		+ 27	86 mins.
		0	18 hrs.
0·2450	1·39	+ 20	1 min.
		+ 10	2 mins.
		0	3 mins.

The acid was stable in pyridine solution, showing $[\alpha]_{5461} + 122·5°$.

The d- and the l-*methyl* ester, prepared in the usual way, crystallised from methyl alcohol or petroleum in needles, m. p. 73—74° (Found : C, 57·4; H, 5·1. $C_{16}H_{16}O_4S_2$ requires C, 57·2; H, 4·8%), $[\alpha]_{5780} \pm 123°$, $[\alpha]_{5461} \pm 145°$ in chloroform ($c = 0·3$), $[\alpha]_{5780} + 128°$, $[\alpha]_{5461} + 148°$ in methyl alcohol ($c = 0·5$).

The first two series of the following figures show the racemisation of the *d*-ester in the presence of sodium methoxide, the methyl-alcoholic solution (made up to 20 c.c.) being examined in a 2 dcm. tube, whilst the third series refers similarly to the *l*-methyl ester of (IX) :

Wt. of ester, g.	Atoms of sodium.	$[\alpha]_{5461}$.	Approximate time, mins., after addition of sodium methoxide.
0·1303	0·08	+ 119°	1
		+ 88	5
		+ 29	21
		0	56
0·1251	0·68	+ 57	1·5
		+ 10	4
		0	5·5
0·0528	0·435	−127	1
		− 53	10
		0	27

The *dl*-ester was recovered from the solution in each case.

α-p-*Carboxyphenylsulphonyl-α-phenylsulphonylethane.*—This was obtained by oxidising the corresponding *dl*-thio-acid with hydrogen peroxide in acetic acid solution on the water-bath during 2 hours. It crystallised from acetic acid; m. p. 244°. The *methyl* ester, prepared by esterification of this acid or by the oxidation of the thio-ester, crystallised from methyl alcohol in small prisms, m. p. 128—129° (Found : C, 52·4; H, 4·7. $C_{16}H_{16}O_6S_2$ requires C, 52·2; H, 4·4%). The ethyl ester had m. p. 84°.

The active acid and methyl esters gave inactive products when they were oxidised in acetic acid with hydrogen peroxide on the water-bath or with permanganate at the ordinary temperature.

α-p-*Carboxyphenylsulphonyl-α-p-tolylsulphonyl-α-phenylthioethane.*—The ethyl ester of (X) gave with sodium ethoxide (1 mol.) in warm alcohol a yellow colour, which was immediately discharged by the addition of diphenyl disulphoxide (1 mol.). After about 1 minute on the water-bath a crystalline solid had separated and the solution was neutral. Water was added, and the crystalline material filtered off and washed with water, m. p. 165°. It was recrystallised from alcohol, in which it was sparingly soluble, and from which it separated in fine needles, m. p. 173° (Found : C, 57·3; H, 4·8. $C_{24}H_{24}O_6S_2$ requires C, 57·2; H, 4·75%).

This *ester* was hydrolysed with excess of alkali in aqueous-alcoholic solution, and the resulting liquid acidified; the acid (X), m. p. and mixed m. p. 233° (ethyl ester, m. p. and mixed m. p. with authentic specimen, 121°), was precipitated. From the mother-liquors, on standing, a small quantity of diphenyl disulphide, m. p. and mixed m. p. 62°, separated. In another experiment the mother-liquors were evaporated and phenylsulphinic acid, m. p. 80°, isolated; this gave diphenyl disulphoxide, m. p. and mixed m. p. 45°, on heating in solution with hydriodic acid. Presumably a sulphenic acid is the first product of hydrolysis and this then gives a di-sulphide and a sulphinic acid, $3Ph\cdot S\cdot OH \rightarrow Ph\cdot S\cdot S\cdot Ph + Ph\cdot SO_2H + H_2O$. Hydrolysis of the ester without further decomposition was effected by using the theoretical amount of alkali, and an acid was then precipitated on acidification, m. p. 190°. After crystallisation from acetic acid it had m. p. 145—147° (Found : C, 53·8; H, 4·9. $C_{22}H_{20}O_6S_3,C_2H_4O_2$ requires C, 53·8; H, 4·5%). The acetic acid in these crystals could not be removed by heating in a vacuum. Crystallisation from methyl alcohol gave fine needles, m. p. 186—190° (decomp.) depending on the rate of heating (Found : C, 55·2; H, 4·5. $C_{22}H_{20}O_6S_3$ requires C, 55·5; H, 4·2%). Recrystallised from acetic acid, this specimen melted at 145°, resolidified, and melted again at 186°. The ethyl ester prepared from this acid had m. p. 173° and was identical with the ester described above.

Resolution of α-p-Carboxyphenylsulphonyl-α-p-tolylsulphonyl-α-phenylthioethane.—The acid (27 g.) and brucine (25 g.) were mixed in alcoholic solution and the sparingly soluble salt which separated (39 g.) was filtered off. It had m. p. 165—170°, $[\alpha]_{5461} - 2\cdot75°$ in chloroform ($c = 6\cdot67$). This salt was repeatedly extracted with hot alcohol insufficient to dissolve it and after six such extractions the residue (6 g.) finally crystallised in prisms, m. p. 171—172° (Found : C, 60·7; H, 5·7; loss at 80° in a vacuum, 2·0. $C_{22}H_{20}O_6S_3,C_{23}H_{26}O_4N_2,H_2O$ requires C, 60·7; H, 5·4; H_2O, 2·0%). $[\alpha]_{5461} + 14\cdot1°$. Further extraction did not alter these values. The acid was obtained from this final fraction by solution in acetic acid, followed by the addition of water. It had a variable m. p. (decomp.) 192—205° according to the rate of heating [Found : C, 55·9, 55·7; H, 4·7, 4·8 (dried at 60° in a vacuum). $C_{22}H_{20}O_6S_3$ requires C, 55·5; H, 4·2%]. $[\alpha]_{5461} - 16\cdot1°$ in acetone ($c = 3\cdot5$). The acid obtained from the salt from the original mother-liquor gave $[\alpha]_{5461} + 15\cdot0°$ in acetone ($c = 4\cdot8$). The d-acid can also be obtained with the aid of the l-menthylamine salt, which crystallises finally from alcohol in small needles, m. p. 220°. The acid from this gave $[\alpha]_{5461} + 15\cdot5°$ in acetone ($c = 0\cdot67$). The l-acid, dissolved in N-sodium hydroxide (1·9 equivs.), gave $[\alpha]_{5461} + 12\cdot2°$ (calc. on acid, $c = 1\cdot7$). No racemisation took place during 18 hours and the recovered acid showed $[\alpha]_{5461} - 15\cdot4°$ in acetone.

The l- and the d-ethyl ester, prepared in the usual way, crystallised from alcohol in needles, m. p. 148°, $[\alpha]_{5461} - 3\cdot2°$ ($c = 1\cdot55$) and $+ 4\cdot24°$ ($c = 4\cdot8$) respectively in chloroform. When equal weights in hot alcohol were mixed, the dl-ester, m. p. 173—174°, crystallised at once. The d-ester, dissolved in chloroform with the addition of sodium ethoxide, was recovered unchanged after an hour. The ester was hydrolysed by aqueous-alcoholic sodium hydroxide (1 equiv.), and the pure active acid recovered unchanged. By using larger quantities of alkali, p-carboxyphenyl-sulphonyl-α-p-tolylsulphonylethane, m. p. 233° (ester, m. p. 121°), was obtained.

Attempts to oxidise the acid and the ester with permanganate and hydrogen peroxide were unsuccessful, as they were either unchanged or broken down into substances soluble in water.

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7. *The Dissociation Constants of Organic Acids. Part XI.* The Thermodynamic Primary Dissociation Constants of Some Normal Dibasic Acids.*

By GEORGE H. JEFFERY and ARTHUR I. VOGEL.

IN spite of numerous determinations of the dissociation constants of dibasic acids by con-ductivity methods during the last 45 years, neither the primary nor the secondary constant of any such acid is known with accuracy, as judged by modern physicochemical standards.

The present communication describes the evaluation of the true primary dissociation constants of certain dibasic acids. The secondary dissociation constants cannot at present be satisfactorily calculated from conductivity data alone (compare Wegscheider, *Monatsh.*, 1902, **23**, 599; Luther, *Z. Elektrochem.*, 1907, **13**, 296; Chandler, *J. Amer. Chem. Soc.*, 1908, **30**, 709; Drucker, *Z. physikal. Chem.*, 1920, **96**, 405; Paul, *ibid.*, 1923, **110**, 434, for methods involving certain arbitrary assumptions); subsidiary transport-number data (compare Sherrill and Noyes, *J. Amer. Chem. Soc.*, 1926, **48**, 1861) or other data obtainable by potentiometric methods are necessary, and these, together with the method of computation, will be discussed in a later paper.

The chief difficulties in the evaluation of the primary dissociation constants are: (1) The determination of the limiting mobility of the acid ion, $l_{0\,HX'}$; direct determination from conductivity data of the acid salt, NaHX or KHX, is impossible owing to the secondary dissociation $HX' \rightleftharpoons H^{\boldsymbol{\cdot}} + X''$; (2) the correction of the conductivity data relating to the disodium salt for hydrolysis. The latter difficulty has been completely overcome, and a method is described (see p. 24) for the application of a combined hydrolysis and solvent correction; μ_0 for the disodium salts can then be calculated by the "n" formula. A very close approximation to the limiting mobility of the acid ion can be obtained as follows: $l_{0\,HX'}$, which for normal dibasic acids is $l_{0\,CO_2H\cdot(CH_2)_x\cdot CO_2'}$, is assumed equal to that of the corresponding amic acid ion, $NH_2\cdot CO\cdot(CH_2)_x\cdot CO_2'$ (Part IX, J., 1934, 1101). The results for the limiting *equivalent* conductivities of the sodium amate and the derived dibasic acid salt, together with the corresponding limiting ionic mobilities, are collected in Table I ($l_{0\,Na^{\cdot}} = 49\cdot 8$; Part IV, J., 1931, 1715).

TABLE I.

	Equivalent conductivity, Λ_0, for		Limiting ionic mobility, l_0, for		
x.	$NH_2\cdot CO\cdot(CH_2)_x\cdot CO_2Na$.	$CO_2Na\cdot(CH_2)_x\cdot CO_2Na$.	$NH_2\cdot CO\cdot(CH_2)_x\cdot CO_2'$, A.	$CO_2'\cdot(CH_2)_x\cdot CO_2'$, B.	$\dfrac{A}{B}$.
1	85·31	114·46	35·5	64·7	0·549
2	81·29	110·75	31·5	60·9	0·517
3	79·83	106·67	30·0	56·9	0·527
4	78·38	102·78	28·6	52·9	0·540
				Mean	0·533

It will be seen that there is a simple connexion between the mobility of the amic and hence of the acid ion and the corresponding neutral-salt ion; the relationship $l_{0\,HX'} = 0\cdot 53 l_{0\,X''}$ may therefore be employed for the calculation of the limiting mobility of the acid ion from that of the derived bivalent ion * (compare Chandler, *J. Amer. Chem. Soc.*, 1908, **30**, 709; also Part IX, *loc. cit.*). Slight variations of this factor do not appreciably affect the value of the true dissociation constant, $K_{1,\,therm.}$ (compare p. 28 for malonic acid).

The true dissociation constant is computed in the usual manner (compare MacInnes, *J. Amer. Chem. Soc.*, 1926, **48**, 2068; MacInnes and Shedlovsky, *ibid.*, 1932, **54**, 1432; Parts VI and VII, J., 1932, 2829; 1933, 1637), Λ_e being given by the expression $\Lambda_{e}\cdot H_2A = \Lambda_{c''}\cdot HCl - \Lambda_{c''}\cdot NaCl + \Lambda_{c''}\cdot NaHA$, where c'' is the ionic concentration, and $\Lambda_{c''}\cdot NaHA$ is computed with the aid of the Debye–Hückel–Onsager equation (for details, see p. 26).

The final results for the thermodynamic dissociation constants and for Λ_0 are tabulated below.

Acid.	Λ_0.	$K_{1,\,therm.} \times 10^5$.	Acid.	Λ_0.	$K_{1,\,therm.} \times 10^5$.
Malonic	383·5	139·7	Adipic	376·6	3·715
Succinic	379·5	6·626	Pimelic	374·6	3·097
Glutaric	378·0	4·535	Suberic	373·1	2·994

* There is an error in the calculations of the mobility of the acid ion from the limiting conductivity of the disodium salt given in Parts I and II (J., 1929, 1476, 1487). The limiting *ionic* conductivity, *i.e.*, $l_{0\,X''}$, of the bivalent ion is derived from the limiting *equivalent* conductivity of the disodium salt by subtraction of the mobility of the sodium ion (compare Glasstone, "The Electrochemistry of Solutions," 1930, p. 68). The published figures for the limiting mobilities of the acid ions must therefore be halved, and the values of $K_{1,\,class.}$ appropriately corrected.

These values are being employed as standards for the investigation of the various potentiometric methods available for the determination of dissociation constants, and the results will be communicated later. The early work of Ostwald, Walden, Voermann, Smith, Bethmann, and others during 1889—1904 on the classical dissociation " constants " of these acids must now be regarded as of very little quantitative value and is not discussed further.

It is necessary to reply to the serious criticisms made by Ives, Riley, and Linstead (J., 1932, 1093) on the work on malonic acid and other dibasic acids described by one of us in Parts I and II (*loc. cit.*). First, referring to the hydrolysis of the disodium salts, they state that " the existence of this hydrolysis introduces a very difficult problem, for it is, at present, impossible to measure this, with anything like the same degree of accuracy as that which can be attained in the measurement of the conductivity of the solutions. Neither can it be calculated from the conductivity data without an accurate knowledge of the mobilities of acid and normal ions," but this criticism has little significance now in view of the methods described in this paper. Secondly, they employ the now generally discarded methods, such as those depending on the Ostwald dilution formula, Kraus's and also Derick's methods, for the evaluation of Λ_0 by the extrapolation of the acid conductivity results, since they hold the view that the high values (approximately 20 units) yielded by extrapolation of the disodium salt data are due to hydrolysis. Although we admit that hydrolysis is undoubtedly present, we do not consider that the discrepancy is to be attributed entirely to this cause. The largest error has been introduced in their calculation of the mobility $l_0 \text{HX}'$. The correct relation is $l_0 \text{HX}' = 0.5 l_0 \text{X}''$, which, for *cyclo*hexane-1 : 1-diacetic acid (*loc. cit.*, p. 1099), is $0.5 \times 42.5 = 21.25$ or $\Lambda_0 = 349.05 + 21.25 = 370.3$, if one employs Ives, Linstead, and Riley's figures, including Λ_0 for the disodium salt, the method of calculation of which is not described.

In view of the foregoing remarks and the fact that those authors have confined themselves to the primary Ostwald dissociation " constants," it would appear that, whilst their main theoretical conclusions may be correct, a determination of the *true* primary and secondary dissociation constants of these cyclic 1 : 1-diacetic acids is desirable.

EXPERIMENTAL.

Preparation of Materials.—Acids. The essential details have already been described (Vogel, J. 1934, 336). All operations were carried out in Pyrex vessels, and all solvents for recrystallisation, indicated in parentheses after the m. p., were of B.D.H. " A.R." purity.

Malonic acid. (I) Kahlbaum's acid. (II) Boots's acid. Both m. p. 136° (decomp.) [benzene-ether–light petroleum (b. p. 60—80°)].

Succinic acid. (I) Kahlbaum's acid. (II) *Ex* nitrile of m. p. 54°. Both m. p. 185—185·5° (acetone).

Glutaric acid. Two specimens, from two independent preparations of the nitrile (b. p. 149—150°/14 mm.), both had m. p. 97·5—98° (chloroform).

Adipic acid. (I) Ethyl succinate, b. p. 113°/22 mm., was reduced with sodium and ethyl alcohol (compare Bennett and Mosses, J., 1931, 1697) to tetramethylene glycol, b. p. 127—129°/12 mm., which was successively converted into the dibromide (b. p. 82—84°/12 mm.) by constant b. p. hydrobromic acid and sulphuric acid (compare Kamm and Marvel, *J. Amer. Chem. Soc.*, 1920, **42**, 307), the dinitrile (b. p. 180—182°/19 mm.) by aqueous-alcoholic potassium cyanide, and into the acid by 50% sulphuric acid; m. p. 151·5—152° (acetone). (II) A commercial specimen, m. p. 151—152° (acetone).

Pimelic acid. From two independent preparations of the dinitrile; b. p. 169—171°/15 mm., m. p. 106° (benzene–ether).

Suberic acid. From two independent preparations of the dinitrile; b. p. 178—180°/15 mm., m. p. 142° (acetone).

Disodium salts. With the exception of Boots's sodium malonate (specimen II), these were all prepared by adding the calculated quantity of sodium hydroxide solution, prepared from the A.R. solid and standardised against A.R. potassium hydrogen phthalate, to known weights of the pure acids, and were recrystallised from aqueous methyl (for the malonate and glutarate) or ethyl alcohol (for the other acids). Details of the preparations are tabulated below.

<div align="center">TABLE III.</div>

C $\times 10^4$.	μ, obs.	$10^6 K_2$ $= 2$.	μ, corr. $10^6 K_2$ $= 3$.	$10^6 K_2$ $= 4$.	C $\times 10^4$.	μ, obs.	$10^6 K_2$ $= 2$.	μ, corr. $10^6 K_2$ $= 3$.	$10^6 K_2$ $= 4$.
1·737	219·17	225·57	224·45	224·14	37·73	202·96	203·16	203·14	203·12
5·148	217·11	218·90	218·76	218·69	57·56	197·37	197·61	197·60	197·59
10·73	213·87	214·69	214·63	214·57	73·35	194·21	194·26	194·26	194·26
22·20	208·41	208·87	208·83	208·77	107·0	189·21	189·21	189·21	189·21

The values at round concentrations, obtained with the aid of a flexible spline, are collected in Table IV for convenience of reference and for comparison with other published data. The concentrations, somewhat extended, used by Kohlrausch and others, have been employed.

<div align="center">TABLE IV.</div>

$C \times 10^4$.	Malonate.	Succinate.	Glutarate.	Adipate.	Pimelate.	Suberate.
5·0	219·10	216·35	210·30	192·40	187·25	184·65
10·0	215·30	213·59	196·90	184·48	183·84	181·30
20·0	209·92	208·90	191·65	183·72	178·18	176·75
30·0	205·81	205·19	187·85	180·30	175·75	173·57
40·0	202·39	202·10	185·06	177·65	173·10	170·98
50·0	199·55	199·31	182·65	175·50	170·90	168·85
60·0	197·12	196·84	180·50	173·70	168·99	167·00
70·0	194·93	194·58	178·70	172·03	167·33	165·40
80·0	193·06	192·55	177·03	170·35	166·02	164·05
90·0	191·35	190·90	175·62	168·90	166·64	162·83
100·0	190·00	189·40	174·38	167·66	163·42	161·65

The True Primary Dissociation Constants.—Λ_e has been deduced from the relation $\Lambda_e H_2A = \Lambda_{c''} HCl - \Lambda_{c''} NaCl + \Lambda_{c''} NaHA$, where c'' is the ionic concentration, for the calculation of which two approximations were sufficient (compare Part VI, J., 1932, 2837) except for malonic acid where three were required. This expression reduces, after substitution of our experimental values for NaCl and HCl (Parts IV and V, J., 1931, 1715; 1932, 400), to $\Lambda_e H_2A = 297·49 + 117·4c''^{0·551} - 1380c''^{0·929} + \Lambda_0 NaHA - xc''^{0·5}$. The last two terms of this expression refer to the acid salt, $\Lambda_0 NaHA = \Lambda_{c''} NaHA + xc''^{0·5}$; $\Lambda_0 NaHA = l_{0 Na·} + l_{0 HA'}$, and for malonic, succinic, glutaric, and adipic acids $l_{0 HA'}$ was assumed to be equal to that of the corresponding amic acid ion, whilst for pimelic and suberic acids it was calculated from the relation $l_{0 HA'} = 0·53 l_{0 A''}$. The value of x was derived from the Debye–Hückel–Onsager equation which at 25° reduces to $\Lambda_0 = \Lambda_{c''} - (0·228\Lambda_0 + 59·8)c''^{0·5}$ (compare Hartley, *Ann. Reports*, 1930, 27, 331; J., 1932, 406). This expression applies to all the normal acids, where c'' is below 1×10^{-3}. For malonic acid, c'' is *ca.* $0·0035N$ at the highest concentration, which is somewhat outside the range of its valid applicability, and this doubtless accounts for the slight decrease of $K_{1, therm.}$ at the highest concentrations. The values deduced for Λ_0 and x are collected in Table V.

<div align="center">TABLE V.

Sodium Hydrogen Salts.</div>

Acid	Malonic.	Succinic.	Glutaric.	Adipic.	Pimelic.	Suberic.
Λ_0	85·3	81·3	79·8	78·4	76·4	74·9
x	79·25	78·35	77·99	77·68	77·22	76·88

In the tabulated results for the acids (Table VI, in which cl. and th. = class. and therm. respectively), G is the concentration in g.-mols./l., μ, obs. is the molecular conductivity to which no solvent correction has been applied (compare Part VI, J., 1932, 2834), $K_{1, class.}$ is the Ostwald ionisation constant, c'' is the ionic concentration, and $K_{1, therm.}$ is the true dissociation constant deduced from the equation $\log K_{1, therm.} = \log K_1' - 1·010 c''^{0·5}$, where K_1' is the dissociation constant computed from the degree of dissociation $\alpha = \Lambda_{c''}/\Lambda_e$. The values of $K_{1, class.}$, although having little significance according to modern electrochemical views since they should, and do, vary with concentration, are included for comparison with old data, and average values have been computed over the higher concentration range where the variation is least. The choice of the values of $K_{1, therm.}$ collected for the calculation of the mean has been influenced by the following considerations. Theory requires that for a monobasic acid $K_{1, class.}$ should increase with rising concentration, but in the present instance, owing to the attendant secondary ionisation, $K_{1, class.}$ falls rapidly at first and then commences to rise at a concentration of *ca.* $0·003$—$0·004N$, whereat it may be assumed that the effect of secondary ionisation is negligible. Hence the values of $K_{1, class.}$ and consequently of $K_{1, therm.}$ possess significance from our viewpoint only after $K_{1, therm.}$ has passed the minimum.

TABLE VI.

True Primary Dissociation Constants.

$C \times 10^4$	μ_e obs.	$K_{1,cl} \times 10^3$	Λ_e	$c'' \times 10^4$	$K_{1,th} \times 10^3$	$C \times 10^4$	μ_e obs.	$K_{1,cl} \times 10^3$	Λ_e	$c'' \times 10^4$	$K_{1,th} \times 10^3$

Malonic acid ($M = 104{\cdot}03$; $\Lambda_0 = 383{\cdot}5$).

Run 1. Cell R. $\kappa = 0{\cdot}691$. Specimen I.

1·626	357·04	(2·047)	372·34	1·5180	(2·081)	58·79	153·21	1·506	378·15	23·4922	1·397
7·541	282·37	(1·550)	382·06	2·8604	(1·514)	84·72	131·24	1·510	377·08	29·4873	1·391
22·28	211·44	(1·513)	380·20	12·3861	(1·430)	107·0	119·63	1·514	376·27	34·0201	1·385
33·93	184·62	(1·502)	379·30	16·4614	(1·412)	122·4	113·45	1·521	375·77	36·8767	1·385

Run 2. Cell Q. $\kappa = 0{\cdot}680$. Specimen II.

3·206	327·67	(1·607)	382·07	2·8070	(1·593)	29·94	191·95	(1·488)	379·60	15·4945	(1·414)
5·262	301·96	(1·534)	381·77	4·2586	(1·501)	46·03	165·58	1·507	378·72	20·5962	1·407
10·43	260·56	(1·502)	381·18	7·2958	(1·414)	55·19	155·10	1·516	378·21	23·1634	1·407
15·40	235·21	(1·498)	380·70	9·7385	(1·413)	65·86	145·24	1·518	377·71	25·9147	1·405

Run 3. Cell V. $\kappa = 0{\cdot}615$. Specimen I.

2·550	338·19	(1·663)	382·19	2·2562	(1·675)	15·03	239·81	(1·568)	380·75	9·4680	(1·500)
5·163	305·04	(1·597)	381·79	4·1250	(1·564)	42·50	170·25	1·506	378·95	19·0912	1·407
8·702	274·71	(1·574)	381·37	6·2680	(1·523)	70·96	141·91	1·507	377·56	26·6715	1·392
								Mean 1·513			Mean 1·397

Succinic acid ($M = 118{\cdot}06$; $\Lambda_0 = 379{\cdot}5$).

Run 1. Cell Q. $\kappa = 0{\cdot}615$. Specimen I.

1·375	191·85	(7·107)	378·55	0·6967	(7·130)	51·95	41·25	6·888	377·50	5·6773	6·590
6·019	107·85	(6·791)	378·31	1·7159	(6·637)	63·81	37·49	6·909	377·38	6·3384	6·593
12·38	79·03	(6·779)	378·13	2·5865	(6·584)	82·39	33·31	6·957	377·21	7·2748	6·618
24·09	58·65	(6·806)	377·90	3·7386	(6·566)	102·1	30·10	6·973	377·04	8·1859	6·613

Run 2. Cell R. $\kappa = 0{\cdot}624$. Specimen II.

3·443	137·53	(7·092)	378·41	1·2514	(6·961)	46·49	43·73	6·897	377·59	5·2617	6·639
9·942	87·68	(6·900)	378·19	2·3048	(6·714)	77·27	34·46	6·996	377·25	7·0530	6·650
17·71	67·67	(6·852)	378·01	3·1701	(6·632)	95·76	31·10	7·004	377·10	7·8968	6·648
34·45	49·79	(6·824)	377·73	4·5406	(6·560)						

Run 3. Cell S. $\kappa = 0{\cdot}626$. Specimen I.

1·890	174·35	(7·242)	378·51	0·8708	(7·278)	18·95	65·77	(6·885)	377·99	3·2972	(6·659)
7·440	100·02	(7·017)	378·27	1·9670	(6·843)	37·90	47·76	6·866	377·66	4·8702	6·622
10·34	86·16	(6·895)	378·19	2·3558	(6·706)	64·48	37·47	6·975	377·35	6·4922	6·653
								Mean 6·941			Mean 6·626

Glutaric acid ($M = 132{\cdot}06$; $\Lambda_0 = 378{\cdot}0$).

Run 1. Cell Q. $\kappa = 0{\cdot}500$. Specimen I.

1·056	194·04	(5·718)	377·12	0·5434	(5·671)	46·46	36·31	4·721	376·28	4·4936	4·530
5·268	99·65	(4·972)	376·92	1·3927	(4·870)	61·89	31·66	4·740	376·17	5·2095	4·538
11·18	71·07	(4·867)	376·77	2·1089	(4·740)	81·04	27·84	4·747	375·95	6·1420	4·531
21·54	52·47	(4·816)	376·59	2·9994	(4·666)	100·5	25·13	4·756	375·85	6·6709	4·533

Run 2. Cell R. $\kappa = 0{\cdot}615$. Specimen II.

3·952	114·81	(5·229)	376·96	1·2029	(5·131)	34·75	41·74	(4·763)	376·39	3·9793	(4·587)
10·10	74·52	(4·887)	376·78	2·0622	(4·761)	47·23	35·98	4·728	376·24	4·6633	4·541
18·16	56·70	(4·864)	376·62	2·8234	(4·658)	70·17	25·28	4·771	375·84	6·8036	4·535
								Mean 4·745			Mean 4·535

Adipic acid ($M = 146{\cdot}08$; $\Lambda_0 = 376{\cdot}6$).

Run 1. Cell Q. $\kappa = 0{\cdot}600$. Specimen I.

0·983	187·05	(4·819)	375·71	0·4894	(4·786).	42·44	34·35	3·860	374·98	3·8757	3·720
5·912	87·32	(4·138)	375·50	1·3746	(4·148)	60·01	29·05	3·869	374·83	4·6502	3·716
11·00	64·87	(3·943)	375·38	1·9007	(3·854)	77·69	25·69	3·879	374·69	5·3259	3·715
21·47	47·38	(3·887)	375·22	2·7105	(3·771)	96·66	23·14	3·888	374·57	5·9715	3·715

Run 2. Cell R. $\kappa = 0{\cdot}612$. Specimen II.

2·501	127·02	(4·317)	375·61	0·8456	(4·228)	50·68	31·48	3·864	374·90	4·2557	3·718
8·188	74·62	(4·010)	375·45	1·6275	(3·946)	69·68	27·05	3·873	373·74	5·0297	3·714
15·33	55·81	(3·952)	375·31	2·2795	(3·844)	90·95	23·89	3·882	374·62	5·8000	3·710
33·23	38·62	(3·894)	375·08	3·4212	(3·762)			Mean 3·873			Mean 3·715

Jeffery and Vogel :

TABLE VI (contd.).

$C \times 10^4$.	μ, obs.	$K_{1,\text{cl.}} \times 10^3$.	Λ_e.	$c'' \times 10^4$.	$K_{1,\text{th.}} \times 10^3$.	$C \times 10^4$.	μ, obs.	$K_{1,\text{cl.}} \times 10^3$.	Λ_e.	$c'' \times 10^4$.	$K_{1,\text{th.}} \times 10^3$.
					Pimelic acid ($M = 160\cdot10$; $\Lambda_0 = 374\cdot6$).						
				Run 1.	Cell Q.	$\kappa = 0\cdot540$.	Specimen I.				
1·249	171·72	(4·848)	373·69	0·5741	(4·797)	51·07	28·70	3·225	372·97	3·9305	3·130
6·495	78·03	(3·560)	373·50	1·3570	(3·488)	69·71	24·84	3·216	372·85	4·5483	3·083
12·54	56·82	(3·402)	373·39	1·9087	(3·318)	89·73	21·78	3·222	372·72	5·2443	3·087
25·00	40·65	(3·302)	373·23	2·7228	(3·202)	110·5	19·71	3·227	372·60	5·8416	3·084
				Run 2.	Cell R.	$\kappa = 0\cdot552$.	Specimen II.				
2·561	121·01	(3·947)	373·63	0·8294	(4·897)	20·20	45·03	(3·313)	373·29	2·4531	(3·219)
7·898	71·02	(3·501)	373·48	1·5014	(3·425)	36·95	33·65	(3·276)	373·10	3·3325	(3·167)
9·214	65·61	(3·424)	373·45	1·6185	(3·348)	45·71	30·25	3·229	373·03	3·6905	3·105
15·15	52·04	(3·389)	373·35	2·1101	(3·302)	79·12	23·17	3·227	372·78	4·9176	3·096
								Mean 3·225			Mean 3·097
					Suberic acid ($M = 174\cdot11$; $\Lambda_0 = 373\cdot1$).						
				Run 1.	Cells R, J, V, N.	$\kappa = 0\cdot595$.	Specimen I.				
1·502	156·16	(4·525)	372·14	0·6303	(4·473)	N 11·02	59·89	(3·382)	371·93	1·7745	(3·302)
4·160	98·20	(3·911)	372·07	1·0977	(3·842)	J 45·05	29·67	3·095	371·55	3·5975	2·987
6·714	76·71	(3·573)	372·00	1·3845	(3·500)	N 78·35	22·81	3·119	371·31	4·8131	2·987
8·602	67·64	(3·453)	371·96	1·5642	(3·377)	V 91·36	21·16	3·121	371·23	5·2046	2·990
11·62	57·98	(3·323)	371·93	1·8115	(3·242)	J 94·82	20·73	3·129	371·21	5·2951	2·996
				Run 2.	Cells R, J, V, N.	$\kappa = 0\cdot612$.	Specimen II.				
2·551	130·31	(4·753)	372·11	0·8790	(4·683)	N 28·89	38·00	(3·336)	371·66	3·0928	(3·229)
5·162	93·02	(4·272)	372·05	1·2903	(3·973)	J 51·41	27·91	3·109	371·49	3·8624	2·998
9·121	64·80	(3·330)	371·95	1·5854	(3·256)	J 69·26	24·21	3·118	371·36	4·5153	2·997
						V 93·24	21·01	3·133	371·22	5·2771	3·001
								Mean 3·117			Mean 2·994

The values of μ at round concentrations are given below :

$C \times 10^4$.	Malonic.	Succinic.	Glutaric.	Adipic.	Pimelic.	Suberic.
1·0	360·00	200·00	195·00	185·00	175·00	165·00
5·0	304·50	118·50	103·00	95·00	85·00	83·00
10·0	265·70	88·10	76·80	67·60	62·90	62·00
20·0	219·50	64·05	54·00	48·40	44·95	44·20
30·0	193·15	53·40	45·40	40·16	37·30	36·50
40·0	175·55	46·60	39·45	35·35	32·40	31·60
50·0	162·35	41·85	35·20	31·90	29·00	28·40
60·0	151·80	38·55	31·95	29·06	26·45	26·00
70·0	142·75	35·80	29·40	26·75	24·50	23·95
80·0	135·30	23·70	27·60	25·03	23·05	22·65
90·0	128·35	31·95	26·15	23·80	21·75	21·20
100·0	121·10	30·80	25·20	22·90	20·65	20·25

The influence of changing the factor from 0·55 to 0·50 in the calculation of the mobility of the acid ion for the extreme case of malonic acid is shown in Table VII ; the effect is small, and will be much smaller for the other normal dibasic acids.

TABLE VII.

$l_{0\,\text{HX}'} = 0\cdot50 \times 64\cdot7 = 32\cdot4$; $\Lambda_0 = 380\cdot4$; Run 1.

$C \times 10^4$.	μ, obs.	$K_{1,\text{class.}} \times 10^3$.	Λ_e.	$c'' \times 10^4$.	$K_{1,\text{therm.}} \times 10^3$.*
1·626	357·04	(2·333)	—	—	—
7·541	282·37	(1·612)	—	—	—
22·28	211·44	(1·549)	—	—	—
33·93	184·62	1·539	376·29	16·5928	(1·445)
58·79	153·21	1·539	375·05	23·6858	1·427
84·72	131·24	1·545	373·97	29·7317	1·425
107·0	119·63	1·544	373·16	34·3829	1·413
122·4	113·45	1·552	372·65	37·1851	1·416
		Mean 1·544			Mean 1·420

* $K_{1,\text{therm.}}$ has been evaluated only over the range where the $K_{1,\text{class.}}$ figures are significant (see above, p. 26).

TABLE VIII.
Sodium Hydrogen Salts.

Sodium hydrogen malonate (M = 126.02).

Run 1 : Cell, Q; κ of water, 0·592; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	1·064	6·124	11·01	22·90	43·68	68·67	85·50	100·2
Λ_e ...	144·20	109·57	102·50	95·54	90·82	87·81	86·69	85·74

Run 2 : Cell, R; κ of water, 0·604; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	3·654	9·473	18·12	33·34	53·53	63·47	92·54
Λ_e ...	118·68	104·75	98·26	93·39	89·00	88·60	86·50

Run 3 : Cell, V; κ of water, 0·604; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	2·811	5·801	9·847	18·85	32·64	60·20
Λ_e ...	121·08	108·44	102·92	96·98	92·84	88·44

Sodium hydrogen succinate (M = 140.04).

Run 1 : Cell, V; κ of water, 0·615; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	1·706	10·74	19·45	45·39	88·32	113·7
Λ_e ...	120·84	94·88	91·74	88·36	85·47	84·29

Run 2 : Cell, Q, κ of water, 0·525; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	1·306	6·001	9·570	16·26	33·01	52·14	61·37	70·62
Λ_e ...	122·84	99·34	95·79	92·81	89·54	87·66	87·02	86·25

Sodium hydrogen glutarate (M = 154.04).

Run 1 : Cell, Q; κ of water, 0·615; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	0·970	6·031	10·13	20·18	42·05	55·66	71·84	87·70
Λ_e ...	133·74	95·29	91·84	87·60	84·25	83·05	81·81	80·84

Run 2 : Cell, R; κ of water, 0·666; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	3·608	10·40	18·46	36·69	72·91	86·23	107·8
Λ_e ...	103·34	92·20	88·40	84·50	81·74	80·89	79·63

Sodium hydrogen adipate (M = 168.07).

Run 1 : Cell, Q; κ of water, 0·540; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	1·545	4·629	13·48	24·20	47·99	70·54	92·35	113·9
Λ_e ...	124·45	101·38	89·22	85·49	82·67	80·98	79·38	78·94

Run 2 : Cell, R; κ of water, 0·593; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	1·544	7·369	14·59	25·74	52·79	71·93	106·3
Λ_e ...	125·24	95·31	88·65	85·82	82·17	80·89	79·04

Sodium hydrogen pimelate (M = 182.09).

Run 1 : Cell, R; κ of water, 0·540; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	1·280	6·244	13·04	26·82	59·36	78·28	94·61	113·6
Λ_e ...	147·25	95·84	88·64	84·81	80·51	79·19	78·15	77·34

Run 2 : Cell, Q; κ of water, 0·612; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	2·510	7·102	11·01	20·15	39·86	61·78	85·10
Λ_e ...	123·98	92·82	89·84	86·18	82·75	80·31	78·58

Sodium hydrogen suberate (M = 196.10).

Run 1 : Cells, R, J, V, N; κ of water, 0·671; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	1·352	3·331	6·138	8·934	12·12	28·07	49·87	65·72
Λ_e ...	155·44	132·27	99·01	90·94	86·64	81·41 J	79·56 N	78·41 V

$C \times 10^4$ ...	66·13	86·38	110·8
Λ_e ...	78·25 J	76·82 N	75·04 V

Run 2 : Cells, Q, J, V, N; κ of water, 0·652; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	2·501	7·342	10·09	13·14	21·12	35·51	54·98	77·61
Λ_e ...	137·34	96·01	97·15	86·00 J	82·94 V	80·57 N	79·05 J	77·52 V

$C \times 10^4$ ...	99·92
Λ_e ...	71·88 N

The *experimental* figures for the sodium hydrogen salts are collected in Table VIII; these were determined (*a*) to provide conductivity data for these substances, and (*b*) for the estimation

of approximate values of K_a, but no satisfactory results were obtained. No solvent correction has been applied, but this will be discussed in a future communication. The stock solutions were prepared by weighing sufficient of the acid to give an approximately $N/10$-solution and then adding the calculated quantity of the disodium salt.

Correction.—The work described in Parts I and II (*loc. cit.*), which includes malonic acid, is subject to the following errors and criticisms : (1) Subtraction of the solvent correction for the acids—no solvent correction is necessary; (2) the density factor in the calculations was reversed; (3) the use of the normal solvent correction for the disodium salts—the correct method of application of a combined solvent hydrolysis correction is described in the present paper; (4) the values for Λ_0 of the acids are high for reasons given in footnote on p. 22; (5) values of $K_{1.\ class.}$ are given at round (interpolated) concentrations : the correct procedure is to use the actual experimental concentrations and to calculate the true dissociation constants, $K_{1.\ therm.}$.

The original results must therefore now be regarded as very approximate, and revised figures for all the acids, calculated in accordance with the methods described in this paper, will be published in the near future.

8. *The Kinetics of the Depolymerisation of Bimolecular Nitrosoisopropylacetone.*

By KENNETH D. ANDERSON and DALZIEL LL. HAMMICK.

BAMBERGER (*Ber.*, 1903, **36**, 685) observed that when a colourless solution of bimolecular nitroso-*tert.*-butane in benzene was exposed for a short time to sunlight, it remained colourless, whereas a portion of the same solution kept for the same time in the dark depolymerised to the deep blue unimolecular form. On warming, or standing in the dark, the colourless solution that had been illuminated also became blue. From these observations, Bamberger concluded that the depolymerisation of the bimolecular nitroso-molecules was arrested by light (" Sonnenlicht hemmt die Depolymerisation der Doppelmolekel "). Bimolecular nitroso*iso*propylacetone, $[CMe_2(NO)\cdot CH_2\cdot CO\cdot CH_3]_2$, was found to behave in a similar manner.

These phenomena appeared sufficiently remarkable to warrant a more detailed investigation, and an account is now given of the kinetics of the thermal (dark) depolymerisation of the second compound, which was chosen in preference to the first because of its greater accessibility. A photochemical study of the substance is not yet complete, but sufficient progress has been made to enable us to state that Bamberger's hypothesis of a polymerisation process catalysed by light is erroneous. Longer exposure of the colourless solutions to light completely destroys the solute, and the explanation of his observations is simply that under suitable conditions the rate of photodecomposition of the blue unimolecular form is greater than its rate of production from the colourless double molecules. A short illumination does not destroy all the nitroso-compound present, and hence blue single molecules are re-formed on warming or standing in the dark.

EXPERIMENTAL.

The rate at which colourless bimolecular nitroso*iso*propylacetone depolymerises in the dark in benzene solution was followed by observing the rate of increase in density of colour due to the production of the blue unimolecular form. This was done by means of a Hilger–Nutting spectrophotometer, in which the absorption tube was mounted in a small brass cylindrical jacket. Water from an electrically controlled thermostat was circulated rapidly through the jacket, and the temperature of the absorption tube maintained constant (thermometer in the jacket) to $\pm$ 0·05°. The whole apparatus was set up in a dark room, and the solutions were illuminated only during the actual process of determining their absorptions.

Before the optical method could be used to study the kinetics of the depolymerisation, it was · necessary to determine the absorption spectrum of the blue unimolecular form for visible light, and also to connect the absorption for the wave-length selected for use in the kinetic measurements with the concentration of the coloured solute. It was possible to obtain this essential preliminary information owing to the fact that depolymerisation of the bimolecular nitroso-compound is complete after a few hours' standing in the dark (Bamberger, *loc. cit.*).

Preparation of Materials.—Nitrosoisopropylacetone, m. p. 75·5°, was prepared according to the method of Bamberger (*loc. cit.*). The solvent was A.R. benzene frozen out three times and distilled from phosphoric oxide in a current of dry air.

The Absorption Spectrum of Nitrosoisopropylacetone.—The data in Table I were obtained for solutions in benzene; under D is given the colour density for light of wave-length λ transmitted by a solution of concentration 0·036 g.-mol./l. in a tube of length 1·95 cm.

<div align="center">TABLE I.</div>

λ, Å.	D.	λ, Å.	D.	λ, Å.	D.	λ, Å.	D.	λ, Å.	D.	λ, Å.	D.
7440	0·222	6950	1·050	6700	1·523	6450	1·280	6000	0·641	5500	0·202
7300	0·312	6900	1·196	6650	1·514	6400	1·194	5900	0·554	5400	0·160
7200	0·445	6850	1·332	6600	1·504	6300	1·016	5800	0·452		
7100	0·650	6800	1·425	6550	1·442	6200	0·908	5700	0·378		
7000	0·900	6750	1·488	6500	1·371	6100	0·763	5600	0·284		

It will be seen that maximum absorption occurs at about λ 6700. This line was therefore used in all subsequent experiments.

The Variation of Absorption with Concentration.—The following data were obtained using this line and the same tube, concentrations (C) being given in g.-mol./l.

C	0·0263	0·0374	0·0506	0·0583
D	1·106	1·558	2·152	2·454

The relation between C and D is linear, and is given by $D = 42·1 \times C$.

Velocity Measurements.—Rates of depolymerisation were determined in benzene solution at seven temperatures between 8·09° and 21·86°. Solutions were made up rapidly in solvent maintained at the temperature selected for experiment, and introduced into the jacketed absorption tube ($l = 1·95$ cm.). After a short period to allow thermal equilibrium to be reached, the colour density D was found by means of the spectrophotometer and redetermined after successive intervals of time. Preliminary experiments with pure solvent gave the correction for the absorption due to the benzene, and a short extrapolation of the graph of D against time to zero absorption enabled zero time to be fixed. By means of the relation $D = 42·1 \times C$, where C is the concentration of the unimolecular form, the amount of depolymerisation was obtained. The results, which show that at each temperature the rate of depolymerisation follows a unimolecular law of constant k, are given below; C_0 is the initial concentration of bimolecular form (g.-mol./l.), and t is given in minutes.

Experiments 1 and 2: at 8·09°, with initial concentrations $C_0' = 0·0264M$ and $C_0'' = 0·0346M$; t' and t'' are the respective times for successive fractional changes.

Change, %	10	20	30	40	50	60	70
t'	24	50	82·5	115	154	200	263
t''	23	51	81	113	150	193	250
t (mean)	23·5	50·5	81·8	114	152	196·5	256·8
$k \times 10^3$	4·47	4·41	4·36	4·58	4·56	4·88	4·69

	Expt. 3. $T = 12·1°$. $C_0 = 0·0282$.		Expt. 4. $T = 13·35°$. $C_0 = 0·0287$.		Expt. 5. $T = 14·72°$. $C_0 = 0·0292$.		Expt. 6. $T = 16·0°$. $C_0 = 0·0299$.		Expt. 7. $T = 20·5°$. $C_0 = 0·0294$.		Expt. 8. $T = 21·85°$. $C_0 = 0·0242$.	
Change, %.	t.	$k \times 10^3$.	t.	$k \times 10^3$.	t.	$k \times 10^3$.	t.	$k \times 10^3$.	t.	$k \times 10^3$.	t.	$k \times 10^3$.
10	12	8·76	11·5	9·15	8·5	12·37	7·5	14·02	4	26·30	3	35·08
20	27	8·25	24	9·30	18	12·38	16	13·93	·8	27·89	7	31·88
30	44·5	8·01	38	9·40	27	12·17	25·5	13·98	12	29·76	10·5	34·02
40	63	8·30	53	9·64	42	12·16	36	14·16	18	28·38	15	34·06
50	84	8·24	71	9·99	56·5	12·26	48	14·42	24	28·88	20·5	33·81
60	109	8·41	97·5	9·40	75	12·14	63	14·53	32	28·63	27·5	33·32
70	142	8·47	129	9·33	98·5	12·21	84	14·32	42	28·67	36	33·45

In Table II are given the data necessary for the derivation of the heat of activation of the process of depolymerisation. The values for the viscosity of benzene are taken from the International Critical Tables.

TABLE II.

$T.$	$10^3/T_{\text{abs.}}$	$k \times 10^3.$	$\log 10^3 k.$	$\eta \times 10^3.$	$\log k/\eta.$
8·09°	3·558	4·54	0·6571	7·825	$\bar{1}$·7635
12·1	3·508	8·35	0·9217	7·330	0·0560
13·35	3·492	9·46	0·9750	7·175	0·1192
14·72	3·474	12·23	1·0875	7·035	0·2402
16·00	3·460	14·19	1·1519	6·900	0·3131
20·50	3·407	28·35	1·4526	6·425	0·6448
21·85	3·391	33·58	1·5260	6·320	0·7253

Interpretation of Results.—The graph of log ($10^3 \times k$) against $1/T_{\text{abs.}}$ is a straight line, the slope of which yields a value $E = 24{,}030$ cals. for the Arrhenius heat of activation. The plot of k/η against $1/T_{\text{abs.}}$ is also a straight line, and from its slope we find $E' = 26{,}600$ cals. This will be the true heat of activation on the assumption that each collision between a solvent and a solute molecule with energy equal to E' results in depolymerisation, for then the unimolecular velocity constant will be given by $k = Z . e^{-E'/RT}$, in which $Z = 3\pi\eta\sigma/2m$, the number of solvent–solute collisions per second (Moelwyn-Hughes, " Kinetics of Reactions in Solution," p. 159). On introduction of the values for the viscosity of benzenè at 20°, $\eta = 6·47 \times 10^{-3}$, for the molecular diameter, $\sigma = 8 \times 10^{-8}$ cm., and for $m = (C_6H_{11}O_2N)_2 = 258$, Z is found to be $5·7 \times 10^{12}$, and $e^{-E'/RT} = 1·82 \times 10^{-20}$ very nearly. These data lead to a value for k at 20° of $10·4 \times 10^{-8}$, which is less than the observed value (27×10^{-3}, by interpolation) by a factor of about 10^{-5}. This discrepancy disappears if the energy of activation is regarded as being distributed between a number of internal degrees of freedom of the reacting molecule. Using Hinshelwood's expression (Moelwyn-Hughes, *op. cit.*, p. 163), we find F, which is one less than the number of degrees of freedom involved, to be 4 [since $(E'/RT)^4/\underline{|4} = 1·77 \times 10^{-5}$]. Introducing also the correction for the persistence of velocities (*idem, ibid.*, p. 28), we obtain a calculated value for k at 20° of 24×10^{-3}, as against the observed value of 27×10^{-3}.

9. *The Cathodic Combustion of Hydrogen and Carbonic Oxide.*

By G. I. FINCH.

THE substance of this communication was read in opening a discussion on combustion in electric discharges before the Society in November, 1932. Publication has been delayed pending completion of certain experimental work in progress at that time. The object is to summarise the main results and to draw therefrom the broad conclusions of a series of studies of gaseous combustion in electric discharges carried out by the author and his collaborators since 1925 (see references, p. 39).

Before combustion can be initiated in an inflammable mixture of gases, energy in some form must be furnished from an external source. If heat energy be so supplied, the " ignition temperature " marks the transition point between slow, non-self-propellant combustion and the self-propellant, pre-flame combustion which leads to flame propagation. In the case of electrical energy the term " least igniting energy or current " has a somewhat similar significance. When once set up, the self-propellant stage of combustion is propagated throughout the system independently of the nature of the source of ignition. On the other hand, slow combustion is intimately associated with, and determined by, the energy supply to the combustible system. It is natural, therefore, that the present state of knowledge of the nature and mechanism of gaseous combustion in flame is largely founded upon the study of the pre-ignition stage. In most such experimental inquiries, slow combustion has been brought about by heat, which has, however, certain outstanding disadvantages. For instance, it is difficult to determine the amount of energy expended in inducing and maintaining slow combustion.

Then, whilst flame propagation may be regarded as a homogeneous process, slow combustion supported by an external supply of heat occurs to a greater or lesser extent heterogeneously, *i.e.*, in contact with the reaction vessel, the surface of which may exert such disturbing effects as to obscure the issues. It is true that supposed examples of heat-induced slow combustion have been put forward as occurring homogeneously; but for the most part such claims do not appear to have been substantiated. Also, so far as the author is aware, explosion of a gaseous mixture effected by the transmission of heat through the walls of a containing vessel is always initiated heterogeneously, *i.e.*, at some point where gas and surface, whether solid or liquid, are in contact. Finally, the nature of the radiation emitted shows that the degree to which the component molecules are excited in flame is of a very different and much higher order than that obtaining under the thermal pre-flame conditions of heat-induced slow combustion.

A direct-current discharge between solid electrodes in a gas may take the form of either a low- or a high-tension arc, the essential difference between the two being in the temperature of the cathode. In the first case, the cathode is so hot that electron emission is mainly thermal and the cathode fall of potential is of the order of only 20 volts; in the second case, the cathode is cool, so that electron emission is due to ionic bombardment, and the cathode fall of potential is of the order of several hundred volts. Owing to the necessarily high cathode temperature, a low-tension arc is unsuitable for the experimental study of the slow combustion of gases; but a high-tension arc dissipating energy at a surprisingly high rate can be maintained in a sensitive explosive gaseous mixture without causing ignition (I).

In the high-tension discharge, three luminous zones are ordinarily distinguishable : (i) the cathode and negative glows sheathing the cathode and constituting the cathode zone, (ii) the anode glow, or spot, and finally (iii) the positive column between which and the cathode zone lies the Faraday dark space. The positive column can be wholly suppressed or varied in extent by a suitable choice of gap-width, gas pressure, or current. Reduction of the positive column of a high-tension arc, maintained in an explosive mixture such as, *e.g.*, $2H_2 + O_2$, by decreasing the distance between the electrodes, in no way affects either the anode or the cathode glow, but proportionately reduces the rate of combustion (I). Therefore some combustion occurs in the positive column. Once the positive column has been eliminated, a further reduction in gap-width merely encroaches on the Faraday dark space, but has no effect upon the rate of combustion (I, III). It follows that combustion must be limited to the luminous zones of the discharge.

The rate of combustion in a discharge from which the positive column is absent is directly proportional to the current and independent of the nature of the anode material, but is profoundly affected by that of the cathode (I, III). This remarkable effect cannot be due to a difference in the cathode-potential falls; *e.g.*, dry $2CO + O_2$ burns more than three times as rapidly at a silver cathode ($P.D. = 345$ volts) than at a copper cathode (355 volts) (III). It may therefore be concluded that, in the absence of a positive column, combustion is confined to the cathode zone. Such combustion may conveniently be termed " cathodic combustion."

The cathodic potential fall is independent of either the current or the gas pressure provided, as was throughout the case in the experiments on cathodic combustion now to be considered, the cathode glow be " normal," *i.e.*, free to expand or contract over the electrode surface; thus, since the rate of combustion is directly proportional to the current, it is also similarly related to the rate of energy dissipation within the cathode zone. Also, it is well known that within the range of conditions under consideration, the spectral distribution of energy is determined solely by the nature of the medium in which the discharge is maintained. Thus, from the point of view of the experimental study of gaseous combustion in general, the fact that the rate of cathodic combustion is directly proportional to the discharge current, itself easily measured and controlled, is of the highest importance.

The remarkable effect which the nature of the cathode material can and does exert upon the rate of cathodic combustion might at first sight suggest that such combustion is heterogeneous, *i.e.*, occurs either in part or wholly upon the surface of the cathode.

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Such a view is, however, at once negatived by the following facts : The area of the electrode surface enveloped by the cathode glow increases with either increasing current or decreasing gas pressure (I), but the rate of cathodic combustion of a given gaseous mixture is directly proportional to the current and, in the case of hydrogen–oxygen or carbon monoxide–oxygen mixtures in their combining proportions, is also practically independent of the pressure (I, III).   On the other hand, with certain mixtures an increase in pressure may result in either an increase or a decrease in the rate of combustion, depending in the main upon the nature of their composition (VI, VII, VIII).   Thus the rate of cathodic combustion is in no way determined by the area of electrode surface enclosed by the cathode glow.   Finally, a change in pressure by itself affects, not only the extent of cathode area enveloped by the cathode glow, but also the thickness of the glow (I) without, however, necessarily affecting the rate of combustion (I, III).   In view of these facts, it seems reasonable to conclude that cathodic combustion does not take place, even in part, at the immediate surface of the electrode, but is confined to the cathode zone. These considerations, in conjunction with the fact that the cathode material can and does greatly affect the rate of combustion, strongly suggest that the specific effect of the nature of the cathode material must be due to something projected away from the electrode surface into the cathode zone, where alone its influence is felt.

A dry $2CO + O_2$ mixture burns approximately five times faster at a silver, gold, platinum, or palladium cathode than at one consisting of either tantalum or tungsten (III). It will at once be recognised that this order also divides these metals into two classes, according to whether they are good or indifferent cathodic sputterers.   Further examples of these two groups of metals have been examined, and without exception it has been found that dry carbon monoxide–oxygen mixtures always burn more readily at a freely sputtering cathode than at a poor sputterer (III, VI).   We may, therefore, conclude that the specific effect of the nature of the cathode material is due to the presence within the cathode zone of metal particles emanating from the cathode.   There is evidence to show that such metal is projected into the cathode zone, not in the form of aggregates, but as discrete atoms.   Thus, (i) the spectrum of the cathode glow in $2CO + O_2$ burning at silver exhibits the line spectrum of this metal (V) ; (ii) an electron beam traversing a jet of magnesium, aluminium, or zinc vapour is randomly scattered (XI) ; (iii) the crystal structure of a film formed by the condensation of aluminium vapour is profoundly affected by the nature of the substrate (XI), which could hardly be the case if appreciable aggregation of atoms had taken place prior to deposition ; (iv) finally, the crystal size of platinum films formed by cathodic sputtering decreases with increasing rate of sputtering, until practically all sign of organised crystal structure is lost (XII, XIII).   In the light of these facts, it may be concluded that the specific effect of the nature of the cathode material upon the rate of cathodic combustion is due to the presence within the cathode zone of atoms of the metal of which the electrode consists, and that cathodic combustion is a purely homogeneous process, all reactions occurring in the gaseous phase.

Dry $2CO + O_2$ burns slowly at a tantalum or tungsten, *i.e.*, non-sputtering, cathode (Fig. 1) ; but at a freely sputtered cathode, such as gold or silver, the metal atoms projected into the cathode zone effect an approximately five-fold (Fig. 1) increase in the rate of combustion of the dry mixture (III), and a similar remarkable acceleration (Fig. 1) is brought about by the addition of water vapour (IV).   The accelerating effects of steam and metal atoms are, however, not additive, for the presence of moisture slightly reduces the rate of combustion of a $2CO + O_2$ mixture at a sputtering cathode (IV).   Furthermore, the rôles played by steam and metal atoms in overcoming the reluctance of carbonic oxide to burn cathodically must differ fundamentally, because steam is most active in accelerating the combustion of mixtures rich in carbonic oxide, whereas the rate of combustion of carbonic oxide at a freely sputtering cathode attains a maximum when excess oxygen is present (VI, VII) (Fig. 1), whilst replacement of the excess of oxygen by helium or argon mainly results in a dilution effect (VI).   Finally, the independent modes of activity of steam and metal atoms in promoting the combustion of carbonic oxide–oxygen mixtures is established by the results recorded graphically in Fig. 2 ; when both steam and metal particles are present, the curve showing the relation between rate of cathodic

combustion and mixture composition exhibits two characteristic maxima, the one due to moisture where carbonic oxide is in excess, and the other due to sputtered metal in oxygen-rich mixtures (VI, VII). Thus, steam and metal atoms do not interfere to any pronounced extent with each other in promoting the cathodic combustion of carbonic oxide–oxygen mixtures.

From these facts and considerations, the following general conclusions relating to the cathodic combustion of carbonic oxide may be drawn : (i) Carbonic oxide has great difficulty in combining directly with oxygen; (ii) metal atoms overcome the reluctance of carbonic oxide to burn by acting in some manner with oxygen and rendering it suitable for easy interaction with carbonic oxide; finally, (iii) steam or some product of its decomposition by the discharge promotes the combustion by reacting with carbonic oxide. These general conclusions can now be examined more closely in the light of the further experimentally established facts set forth below.
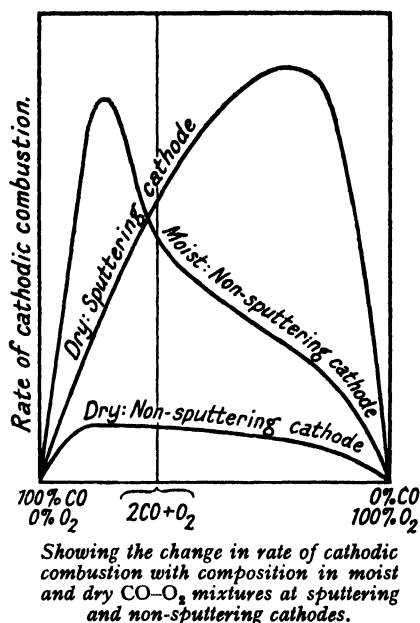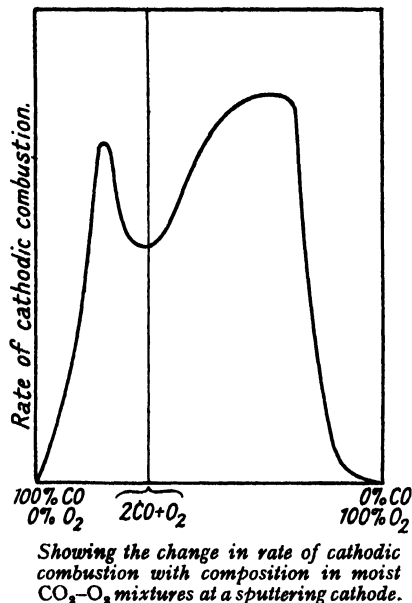

Fig. 1.

Showing the change in rate of cathodic combustion with composition in moist and dry CO–O$_2$ mixtures at sputtering and non-sputtering cathodes.

Fig. 2.

Showing the change in rate of cathodic combustion with composition in moist CO$_2$–O$_2$ mixtures at a sputtering cathode.

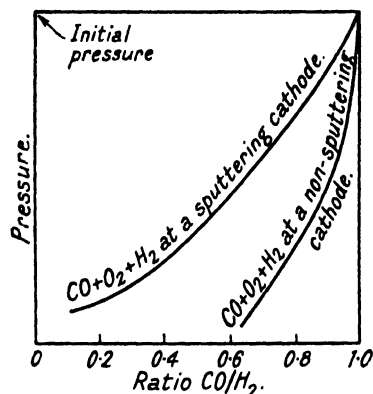Note.—*Figs.* 1, 2, *and* 4 *are to the same scale.*

Dry, arced carbonic oxide exhibits the phenomenon of after-glow, and oxygen does so likewise (X). Oxygen in the state of after-glow contains ozone in abundance (X). In spite of the high levels of excitation which the colours of the after-glows indicate, and in spite of the fact that the glowing oxygen contains ozone, no combustion occurs on mixing such streams of carbonic oxide and oxygen (X).

When pure dry carbonic oxide circulates through the cathode zone, carbon dioxide is formed and carbon is deposited in equivalent amount, mainly on the cathode (VI). The ' CO ' band, but not the Swan spectrum, is emitted (V). It may therefore be concluded that under these conditions auto-oxidation occurs as follows : $CO + CO = CO_2 + C$. The rate of such auto-oxidation is about three times less than that of the combustion of dry $2CO + O_2$ at a non-sputtering cathode (VI). No carbon deposition is to be observed on the cathode enveloped by the cathode zone during the combustion of carbonic oxide–oxygen mixtures containing not less than about 10% of the latter (VI). Thus it would appear that carbon formed by the auto-oxidation of carbonic oxide is burnt too rapidly by oxygen to permit of its escape from the cathode zone and subsequent deposition upon the cathode in any except carbonic oxide–oxygen mixtures greatly deficient in oxygen. We may therefore conclude that the mechanism of the cathodic combustion of carbonic

oxide with oxygen in the absence of sputtered metal atoms consists, at least in part, of the auto-oxidation of carbonic oxide and the subsequent combustion of the carbon thus set free. So far the study of the cathodic combustion of carbonic oxide has afforded no proof of the possibility or otherwise of the direct oxidation of carbonic oxide by oxygen. This does not warrant, however, the assumption that any such direct union is impossible; the evidence on this point must be regarded as neutral, in so far as concerns cathodic combustion.

Thin films of an oxide of platinum exhibiting little or no crystal structure can be formed by cathodic sputtering in oxygen under suitable conditions of pressure and current. Films sputtered under similar conditions, but in oxygen-free hydrogen, nitrogen, or argon, however, consist mainly of relatively large crystals of platinum (XII). Thus, platinum atoms are chemically active in that they readily combine with oxygen to form an oxide which exhibits little tendency to aggregate, whereas platinum atoms by themselves tend to group into crystals. The platinum oxide films are more or less readily reduced by hydrogen at room temperature (XII, XIII), and carbonic oxide exerts a similar but far more sluggish action (XII). Such films are almost instantaneously reduced by a cool stream of dry, arced hydrogen or carbonic oxide (X). The reduction is accompanied by a pronounced, sometimes even remarkable, increase in crystal size (XII, XIII). In view of these results and of the fact that sputtered metal atoms are most active as promoters of cathodic combustion when oxygen is in excess (VI), it seems reasonable to conclude that the metal acts by forming oxides or unstable metal atom–oxygen complexes which are readily reduced by suitably excited carbonic oxide.

Carbonic oxide–oxygen–hydrogen mixtures containing not more than sufficient oxygen for complete combustion burn at either non-sputtering or sputtering cathodes in such a manner that carbon dioxide is more rapidly formed than is steam (VII) (Fig. 3); thus, the carbonic oxide appears to burn more rapidly than does the hydrogen. The rates of cathodic combustion occurring in such mixtures at non-sputtering cathodes have, however, little or nothing in common with those observed in the case of either dry or moist carbonic oxide–oxygen mixtures; $CO–O_2–H_2$ mixtures burn, in general, not only much faster, but the manner in which the rate of combustion varies with increasing combustible contents also bears no resemblance to that observed in the case of dry or moist $CO–O_2$ mixtures (VI, VII) (Fig. 1). A close parallel exists, however, between the rates of cathodic combustion of $CO–O_2–H_2$ and $H_2–O_2$ mixtures; in both, the rates of combustion at a non-sputtering cathode increase rapidly and in a similar manner with increasing combustible contents (VII, VIII, IX) (Fig. 4). Furthermore, within the limits hitherto examined, a partial substitution of carbonic oxide by an equivalent amount of hydrogen has little or no effect upon the rate of combustion of $CO–O_2–H_2$ mixtures. In view of these facts, it is difficult to resist the conclusion that, during the combustion of $CO–O_2–H_2$ mixtures at a sputtering cathode, the hydrogen burns first and at a rate which in effect determines that of the mixture as a whole, and that the apparent preferential combustion, *i.e.*, the more rapid disappearance of carbonic oxide, is due to oxidation by some product, or products, of the combustion of hydrogen which is thereby returned to the mixture; and, further, since the rate at which carbonic oxide burns when undergoing such preferential combustion is much higher than that observed in the case of dry carbonic oxide–oxygen mixtures, it follows that carbonic oxide is burnt far more readily by the product, or products, of the combustion of hydrogen than by oxygen.
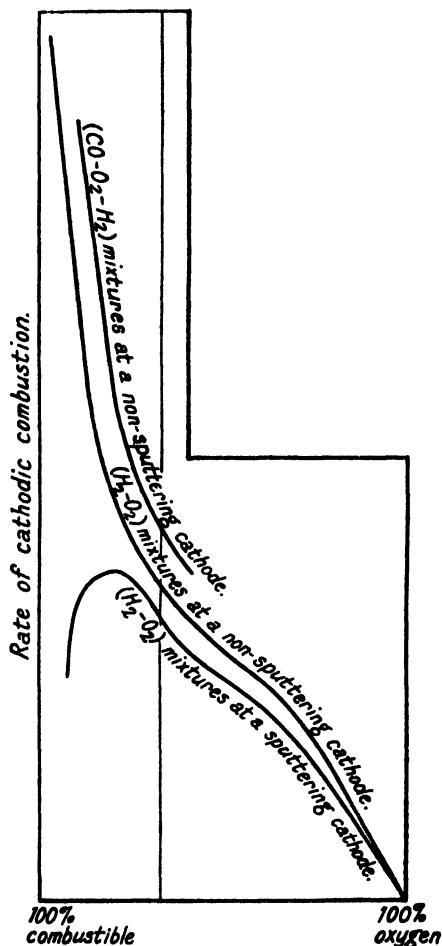
The extent to which carbonic oxide burns preferentially in $CO–O_2–H_2$ mixtures is far greater when combustion proceeds at a sputtering cathode than otherwise (Fig. 3), although

FIG. 3.

Showing that carbonic oxide disappears more rapidly than does hydrogen as cathodic combustion proceeds in a CO + O_2 + H_2 mixture.

the total rate of combustion is greatly reduced, in some cases by as much as three times, by the presence of metal atoms (VII). These facts strongly suggest that (i) carbonic oxide is burnt by at least two oxidation products of hydrogen, one of which is more highly oxygenated than the other, and thus, on reduction, leads to the return of less hydrogen, and that (ii) metal atoms either prevent the formation of, or decompose, the oxygen-rich hydrogen combustion product, and in this manner not only increase the extent to which the carbonic oxide is burnt preferentially, but are also responsible for the reduction in the rate of combustion observed at a sputtering cathode. This view is further supported by the fact that H_2–O_2 and CO–O_2–H_2 mixtures containing combustible in sufficient excess all burn at a sputtering cathode at a practically similar rate, which is, within wide limits, independent of the composition (VII, VIII). Thus the conclusion may be drawn that the dominating mechanism in the combustion of CO–O_2–H_2 mixtures at either sputtering or non-sputtering cathodes is that of the combustion of hydrogen, in the sense that in such mixtures the oxidation of carbonic oxide is effected by oxidation products of hydrogen and is thus determined mainly by the prior combustion of hydrogen.

In addition to steam, the only oxidation products of hydrogen known to be formed within the cathode zone maintained in either steam or electrolytic gas are hydroxyl and, possibly, hydrogen peroxide, which has been detected, though only in small amounts, in the products issuing from the discharge (VI, VII, VIII). Hydroxyl, however, is present in profusion (V). It is well known that finely divided metals are capable of decomposing hydrogen peroxide, sometimes even explosively. Nevertheless, it is improbable that hydrogen peroxide plays any material rôle in the cathodic combustion of CO–O_2–H_2 mixtures, because moist CO–O_2 mixtures deficient in oxygen burn at rates which are not only practically independent of the presence, or otherwise, of metal atoms, but are also much higher than the rates of combustion at a sputtering cathode of similar mixtures in which the steam has been replaced by an equivalent amount of hydrogen (VI and VII); and it can hardly be supposed that hydrogen peroxide is more liable to decomposition by metal atoms when produced directly from hydrogen than when formed in any other manner. These facts do, however, strongly

FIG. 4.

Showing the rates of combustion with composition in various mixtures burning at sputtering and non-sputtering cathodes (to scale with Figs. 1 and 2).

suggest that the oxygen-rich combustion product of hydrogen which is so active in burning carbonic oxide is hydroxyl, and that metal atoms neither decompose hydroxyl nor do they prevent its formation from steam; but that sputtered metal in some manner inhibits the formation of hydroxyl as a direct intermediate product of the cathodic combustion of hydrogen to steam.

A view can now be put forward, according to which carbonic oxide can be and is burnt during the cathodic combustion of CO–O_2–H_2 mixtures both by steam and by hydroxyl. Thus, according to this view, the rate of combustion in moist CO–O_2 mixtures deficient in oxygen is independent of the nature of the cathode material, because metal

atoms do not impede the formation of hydroxyl as a result of the decomposition of steam by the discharge. In the case of $CO-O_2-H_2$ mixtures, however, since metal atoms inhibit the formation of hydroxyl from hydrogen, the carbonic oxide is burnt in the main by steam, with the result that the extent to which carbonic oxide burns preferentially in such mixtures is much greater at a sputtering than at a non-sputtering cathode. Finally, it is in the absence of metal atoms that the rate of burning of $CO-O_2-H_2$ mixtures containing excess combustible attains a maximum and the extent of preferential carbonic oxide combustion a minimum, because the oxidation of hydrogen *via* the hydroxyl stage is unhindered, with the result that, not only steam, but also hydroxyl is available to take part in burning the carbonic oxide. The view that carbonic oxide can be and is burnt by two products of the combustion of hydrogen is further supported by the fact that the position of the cathodic water-gas equilibrium is determined mainly by the gas pressure (IX), which suggests that in the one direction equilibrium is approached by two simultaneous reactions, one of which is favoured by an increase in pressure whilst the other is retarded.

Oxygen-rich hydrogen–oxygen mixtures burn at relatively low rates at either a sputtering or a non-sputtering cathode. In the case of mixtures containing excess hydrogen, however, and burning at a non-sputtering cathode, combustion increases at a remarkable rate with increasing hydrogen concentration, an effect which is almost wholly suppressed by the presence of metal atoms (VIII) (Fig. 4). In the first place, these facts strongly suggest that both hydrogen and oxygen must be suitably excited before they can combine, and that the life of oxygen in the excited state is short, whilst that of the hydrogen is long. Further, the more than three-fold reduction in the rate of cathodic combustion which can be and is effected by the presence of sputtered metal atoms can be reasonably explained, in accordance with the view of the mechanism of the combustion of $CO-O_2-H_2$ mixtures put forward above, as follows. Hydroxyl is an intermediate product in the normal combustion of hydrogen to steam. Metal atoms form with oxygen easily reduced oxides or unstable complexes which burn hydrogen to steam directly and thus suppress the intermediate formation of hydroxyl. Finally, since the rate of combustion of a hydrogen-rich hydrogen–oxygen mixture is much greater in the absence than otherwise of metal atoms, *i.e.*, when hydroxyl is freely formed as an intermediate product, it may be concluded that hydroxyl in some manner powerfully promotes the combustion of hydrogen.

The fact that the rates of combustion of H_2-O_2 and of $CO-O_2-H_2$ mixtures at a non-sputtering cathode increase rapidly and in a similar manner with increasing combustible contents (Fig. 4) suggests that the short life of oxygen in the suitably excited state for interaction with hydrogen is due to deactivation by collision with oxygen in some form or other, but not with hydrogen or carbonic oxide. Cool, arced moist hydrogen contains much atomic hydrogen but reacts most reluctantly, if at all, with similarly arced oxygen which is in a state of after-glow and rich in ozone undergoing decomposition (X); thus, the respective levels of excitation to which hydrogen and oxygen must be raised are high if they are to combine directly and without the intervention of any promoter of combustion such as hydroxyl. It is well known, however, that steam dissociates to a measurable extent at comparatively low temperatures of the order of 800°. It follows that the energy required to bring about the decomposition of steam is far less than that necessary in order to excite hydrogen and oxygen sufficiently for them to combine directly. For thermochemical reasons, the most probable initial step in the mechanism of the decomposition of steam consists in the interaction of two steam molecules, whereby hydroxyl and hydrogen are formed. Herein lies a probable explanation of the striking fact, discovered by Smithells, Whitaker, and Holmes (J., 1930, 185), that the ignitability of a $2CO + O_2 + (H_2)$ mixture by an electric discharge is conditioned by a trace of steam. Thus, according to this view, a comparatively powerful discharge is required to ignite the rigidly dried mixture, because the initial formation of hydroxyl calls for the prior excitation of hydrogen and oxygen molecules to relatively high levels; in the case of the incompletely dried mixture, however, a much milder discharge suffices to produce hydroxyl by the decomposition of steam and thus to initiate combustion.

SUMMARY.

The results of a study of the cathodic combustion of hydrogen, carbonic oxide, and of their mixtures with moist and dry oxygen, are reviewed. It is concluded that the following reactions occur during the cathodic combustion.

(i) Dry $CO-O_2$ mixtures in the absence of metal atoms :

    (a) $2CO = CO_2 + C$,

    (b) C is burnt by oxygen.

(ii) Dry $CO-O_2$ mixtures in the presence of metal atoms :

    (a) Me + Oxygen = MeO, an unstable metal oxide,

    (b) $CO + MeO = CO_2 + Me$.

(iii) Moist $CO-O_2$ mixtures :

    (a) $CO + H_2O = CO_2 + H_2$.

(iv) $CO-O_2-H_2$ mixtures in the absence of metal atoms :

    (a) H_2 burns *via* OH to H_2O,

    (b) $CO + OH = CO_2 + H$,

    (c) $CO + H_2O = CO_2 + H_2$.

(v) H_2-O_2 mixtures in the absence of metal atoms : When the mixture is rigidly dried the initial step is (a) $H_2 + O_2 = 2OH$, but (b) $2H_2O = 2OH + H_2$ when moisture is present ; whereupon hydroxyl in some manner acts as a powerful promoter in the succeeding stages of combustion.

(vi) H_2-O_2 mixtures in the presence of metal atoms :

    Me + Oxygen = an unstable metal oxide,

    $H_2 + MeO = H_2O + Me$.

It is not suggested that these views afford a complete explanation of the modes of combustion of hydrogen and carbonic oxide; in view of the close parallel which can be drawn between the conditions of gaseous combustion in the cathode zone and in flame, however, it is submitted that the new facts brought to light by the study of cathodic combustion must be taken into account in any attempt to formulate a considered view of the mechanisms of the combustion of hydrogen and carbonic oxide, and of the rôle played therein by steam.

The author expresses his indebtedness to his collaborators whose names appear in the following list of references : I, Finch and Cowen, *Proc. Roy. Soc.*, 1926, **111**, *A*, 257; II, *idem, ibid.*, 1927, **116**, *A*, 529; III, Finch and Hodge, *ibid.*, 1929, **124**, *A*, 303; IV, *idem, ibid.*, 1929, **125**, *A*, 532; V, Finch and Thompson, *ibid.*, 1930, **129**, *A*, 314; VI, Finch and Patrick, *ibid.*, p. 656; VII, *idem, ibid.*, p. 672; VIII, Finch and Mahler, *ibid.*, 1931, **133**, *A*, 173; IX, Finch, Bradford, and Greenshields, *ibid.*, 1934, **143**, *A*, 482; X, Finch and Bradford, J., 1934, 360; XI, Finch and Quarrell, *Proc. Roy. Soc.*, 1933, **141**, *A*, 398; XII, Finch, Murison, Stuart, and Thomson, *ibid.*, p. 414; XIII, Finch and Ikin, *ibid.*, 1934, **145**, *A*, 551.

10. *Some Physical Properties of the Alkyl Compounds of Mercury, Tin, and Lead.*

By W. J. JONES, D. P. EVANS, T. GULWELL, and D. C. GRIFFITHS.

AN investigation of the gradation of physical properties in the series of alkyl compounds of mercury, tin, and lead has been made on lines similar to those already carried out in the case of the compounds of phosphorus, arsenic, antimony, and bismuth (J., 1930, 1310;

1931, 2109; 1932, 2284; *Bull. Soc. chim.*, 1931, **49**, 187; *J. Physical Chem.*, 1933, **37**, 583).
In the present work it has been necessary to prepare a number of new members of each series, and in order further to characterise these compounds, certain of their derivatives have been prepared also.

In this paper, formulæ for the b. p. and molecular volume of a mercury, tin, or lead alkyl are given. It has been found that the atomic refractivities, for D light, of mercury, tin, and lead, when attached to primary alkyl groups, are 12·84, 13·87, and 18·33, respectively. Optical exaltation is exhibited where *sec.*- and *tert.*-alkyl groups are present. The heats of formation of the mercury and tin compounds rise regularly as the *n*-alkyl series are ascended, but the heats of formation of compounds containing secondary alkyl groups differ considerably from those of the compounds containing the corresponding primary alkyl groups.

EXPERIMENTAL.

Mercury Dialkyls.—Di-n-*amylmercury* (Found : C, 35·3; Hg, 58·7. $C_{10}H_{22}Hg$ requires C, 35·0; Hg, 58·5%) was obtained by the interaction of 180 g. (0·5 mol.) of mercuric bromide, gradually added, and a solution of *n*-amylmagnesium bromide (2 mols., 48 g. of magnesium, 258 c.c. of *n*-amyl bromide, and 1500 c.c. of ether) that had been filtered through glass-wool in hydrogen. The mixture was refluxed and mechanically stirred for 15 hours and then 1000 c.c. of water were added. The whole was filtered to remove precipitated *n*-amylmercuric bromide, and the ethereal layer was separated and dried over calcium chloride. The ether was evaporated, and the residue of di-*n*-amylmercury, *n*-decane, and *n*-amylmercuric bromide filtered off. The filtrate was washed with a small quantity of cold absolute alcohol, the heavy layer being then run off and treated with an excess of alcoholic silver nitrate. Ether (400 c.c.) was added, and the mixture was again filtered. In this way all traces of *n*-amylmercuric bromide were removed. The ethereal layer was then separated, dried, and fractionally distilled under low pressure. The residue left after removal of ether gave 24 c.c. of *n*-decane and 36 g. of di-*n*-amylmercury, b. p. 106°/0·5 mm.

When treated with iodine, di-*n*-amylmercury forms n-*amylmercuric iodide* (Found : I, 31·6; Hg, 50·7. $C_6H_{11}IHg$ requires I, 31·9; Hg, 50·3%). n-*Amylmercuric thiocyanate* (Found : Hg, 61·0; CNS, 17·6. $C_6H_{11}NSHg$ requires Hg, 60·8; CNS, 17·6%) was obtained as an insoluble, white powder, m. p. 108°, by treating an alcoholic solution of *n*-amylmercuric hydroxide with ammonium thiocyanate.

Di-dl-*amylmercury* (Found : C, 34·9; Hg, 58·3. $C_{10}H_{22}Hg$ requires C, 35·0; Hg, 58·5%) was prepared by refluxing a solution of *dl*-amylmagnesium bromide (2 mols.) with mercuric bromide (0·5 mol.) for 15 hours. Fractionation of the ethereal extract yielded the dialkylmercury, b. p. 93°/1 mm. Treatment with silver nitrate solution was unnecessary in this preparation, as no *dl*-amylmercuric bromide passed over during the fractionation. dl-*Amylmercuric bromide* (Found : Br, 23·1; Hg, 56·5. $C_6H_{11}BrHg$ requires Br, 22·8; Hg, 57·0%) separated as a by-product in the preparation of di-*dl*-amylmercury; it forms white plates, m. p. 119°, from alcohol. dl-*Amylmercuric iodide* (Found : I, 31·4; Hg, 50·2. $C_6H_{11}IHg$ requires I, 31·9; Hg, 50·3%), obtained by treating di-*dl*-amylmercury first with alcoholic and then with solid iodine, forms white plates from alcohol, m. p. 128°. dl-*Amylmercuric sulphate* (Found : Hg, 62·4; SO_4, 15·1. $C_{10}H_{22}O_4SHg_2$ requires Hg, 62·7; SO_4, 15·3%), from *dl*-amylmercuric hydroxide and dilute sulphuric acid, forms shiny, white plates from water, m. p. 180° (decomp.).

Di-n-*hexylmercury* (Found : Hg, 53·7. $C_{12}H_{26}Hg$ requires Hg, 54·1%) was prepared by refluxing *n*-hexylmagnesium bromide (2 mols.) solution with mercuric bromide (0·5 mol.) for 21 hours. Purification as described for the *n*-amyl compound gave 18 g. of di-*n*-hexylmercury, b. p. 110—112°/0·5 mm., 90 g. of *n*-hexylmercuric bromide, and 42 c.c. of *n*-dodecane, per 48 g. of magnesium used.

Whitmore, Hansen, and Carnahan (*J. Amer. Chem. Soc.*, 1929, **51**, 894) and Beattie and Whitmore (*ibid.*, 1933, **55**, 1571) have shown that, when an alkali alkoxide dissolved in the corresponding alcohol is refluxed with an arylmercuric halide, there is formed the diarylmercury. A similar reaction was observed in the present work on treating *n*-butylmercuric bromide with sodium *n*-propoxide in *n*-propyl alcohol. Sodium (1·5 g.) was dissolved in 100 c.c. of *n*-propyl alcohol, and 15 g. of *n*-butylmercuric bromide were added. The mixture was boiled gently for 5 mins., cooled, and filtered. The excess alcohol was removed by distillation under low pressure. The brown, pasty residue, on being heated under low pressure, yielded a fraction distilling at 80—140°/0·5 mm.; during the distillation some decomposition occurred with

separation of metallic mercury. Redistillation of this fraction yielded 6 g. of di-*n*-butylmercury, b. p. 105°/10 mm., which was further identified by its conversion into *n*-butylmercuric iodide, m. p. 116° (from alcohol).

The carbon in the organo-mercuric compounds was determined by combustion, the mercury and water being eliminated by condensation in a cooled U-tube, and the carbon dioxide being passed, through a sulphuric acid and pumice U-tube, into a potassium hydroxide absorption vessel for weighing. The mercury in its dialkyls was determined by the methods of Volhard (*Annalen*, 1892, **267**, 172) and Koten and Adams (*J. Amer. Chem. Soc.*, 1924, **46**, 2764), in its alkyl bromides by the method of Kharasch and Flenner (*ibid.*, 1932, **54**, 686), but that in its alkyl iodides by the following new method. A mixture of 20 c.c. of fuming sulphuric acid and 10 c.c. of fuming nitric acid was added in the cold to 0·3 g. of the alkylmercuric iodide. Then the dropwise addition of 20 c.c. of water developed sufficient heat to effect complete decomposition of the iodide. An excess of solid sodium carbonate and 50 c.c. of water added to the solution precipitated mercuric iodide, which was then redissolved by adding a dilute solution of potassium iodide. The brown colour that developed was destroyed by rendering the solution neutral or very slightly acid with sulphuric acid and then boiling. On addition of fresh ammonium sulphide solution, mercuric sulphide was quantitatively precipitated.

Tin Tetra-alkyls.—Tetra-n-butyltin (Found : C, 55·3; H, 10·3; Sn, 34·1. $C_{16}H_{36}Sn$ requires C, 55·3; H, 10·5; Sn, 34·2%) was prepared by the action of a benzene solution of 64 g. of anhydrous stannic chloride upon the cooled Grignard reagent from 48 g. of magnesium, 216 c.c. of *n*-butyl bromide, and 1200 c.c. of ether. To the product were added 200 g. of ammonium chloride in 1000 c.c. of water, and the ethereal layer was separated, filtered, dried, and fractionally distilled under low pressure. There were thus obtained 8 g. of *n*-octane, b. p. 18°/10 mm., and 50 g. of pure tetra-*n*-butyltin, b. p. 145°/10 mm. after repeated fractionation. The tin in the tetra-alkyls was determined by decomposition with fuming nitric acid in a sealed tube, and weighing as stannic oxide. *Tri-n-butyltin bromide* (Found : Br, 21·5. $C_{12}H_{27}BrSn$ requires Br, 21·6%), b. p. 163°/12 mm., was obtained in good yield by slowly dropping bromine (2 atoms per atom of tin) on to tetra-*n*-butyltin and distilling the product. *Tri-n-butyltin iodide* (Found : I, 30·4. $C_{12}H_{27}ISn$ requires I, 30·4%) was prepared by adding 13 g. of iodine in 100 c.c. of carbon tetrachloride to 18 g. of tetra-*n*-butyltin. After a day, the product was fractionated, giving 18 g. of the iodide, b. p. 172°/10 mm.

The following stannanes and derivatives were prepared and purified as in the case of the *n*-butyl compounds : *tetra-n-amyltin* (Found : C, 59·3; H, 10·9; Sn, 29·2. $C_{20}H_{44}Sn$ requires C, 59·5; H, 11·0; Sn, 29·4%), b. p. 181°/10 mm.; *tetra-dl-amyltin* (Found : C, 59·2; H, 10·9; Sn, 29·4%), b. p. 174°/10 mm.; *tetra-n-hexyltin* (Found : C, 62·7; H, 11·3; Sn, 25·8. $C_{24}H_{52}Sn$ requires C, 62·7; H, 11·4; Sn 25·9%), b. p. 209°/10 mm.; *tetra-n-heptyltin* (Found : C, 65·4; H, 11·8; Sn, 22·9. $C_{28}H_{60}Sn$ requires C, 65·3; H, 11·7; Sn, 23·0%), b. p. 239°/10 mm.; *tetra-n-octyltin* (Found : C, 67·4; H, 12·0; Sn, 20·7. $C_{32}H_{68}Sn$ requires C, 67·2; H, 12·0; Sn, 20·8%), b. p. 268°/10 mm.; *tetra-β-phenylethyltin* (Found : C, 71·5; H, 6·8. $C_{32}H_{36}Sn$ requires C, 71·2; H, 6·7%), b. p. 288°/12 mm.; *tri-n-amyltin bromide* (Found : Br, 19·6. $C_{15}H_{33}BrSn$ requires Br, 19·4%), b. p. 189°/13 mm.; *tri-n-amyltin iodide* (Found : I, 27·7. $C_{15}H_{33}ISn$ requires I, 27·7%), b. p. 198°/15 mm. *Di-n-propyltin dibromide* (Found : Br, 43·8; Sn 31·9. $C_{6}H_{14}Br_{2}Sn$ requires Br, 43·8; Sn, 32·6%) was prepared by dissolving 18 g. of tetra-*n*-propyltin in carbon tetrachloride, cooling in ice, and adding 6·2 c.c. of bromine dissolved in the same solvent. On the next day another solution of 6·2 c.c. of bromine was added. On concentration of the solution, the dibromide separated as a white, crystalline solid, m. p. 53° (recryst.).

Several new mixed alkyltins were prepared by the interaction of trialkyltin bromides with Grignard reagents, and were isolated and purified as described for the tetra-alkyltins. *Methyltri-n-propyltin* (Found : C, 45·5; H, 9·2. $C_{10}H_{24}Sn$ requires C, 45·6; H, 9·2%), b. p. 93°/10 mm., $d_{4}^{20°}$ 1·1404; *tri-n-propyl-n-butyltin* (Found : C, 51·1; H, 9·9. $C_{13}H_{30}Sn$ requires C, 51·2; H, 9·9%), b. p. 121°/10 mm., $d_{4}^{20°}$ 1·0908; *methyltri-n-butyltin* (Found : C, 51·2; H, 9·9. $C_{13}H_{30}Sn$ requires C, 51·2; H, 9·9%), b. p. 121°/10 mm.; *ethyltri-n-butyltin* (Found : C, 52·5; H, 10·2. $C_{14}H_{32}Sn$ requires C, 52·7; H, 10·1%), b. p. 129°/10 mm.; *n-propyltri-n-amyltin* (Found : C, 57·5; H, 10·7. $C_{18}H_{40}Sn$ requires C, 57·6; H, 10·7%), b. p. 163°/10 mm.

Lead Tetra-alkyls.—An ethereal solution containing tri- and tetra-*n*-butyl-lead was obtained by the interaction of lead chloride with excess of *n*-butyl Grignard reagent, the mixture being refluxed for 3 hours until the colour became greenish-yellow. The mixture, having been cooled, was treated with ice-water, and the ethereal layer was separated, dried over calcium chloride, and then saturated at −10° with chlorine. *Di-n-butyl-lead dichloride* (Found : Cl, 18·1; Pb, 52·8. $C_{8}H_{18}Cl_{2}Pb$ requires Cl, 18·1; Pb, 52·8%) separated from the solution, and, after being

washed, was recrystallised from alcohol. From 380 g. of lead chloride there were obtained 100 g. of the organic dichloride, which formed shiny, pale yellow plates, decomp. 108°. Di-*n*-butyl-lead dibromide (Found : Pb, 42·9. Calc. for $C_8H_{18}Br_2Pb$: Pb, 43·0%) was obtained in 80% yield by treating di-*n*-butyl-lead dichloride, suspended in cold alcohol, with excess of silver oxide, filtering the mixture, and adding excess of dilute hydrobromic acid to the clear filtrate. The bromide forms pale yellow needles from alcohol, which sinter and turn white at 110°. This compound has been previously made by Danzer (*Monatsh.*, 1925, **46**, 241), but no m. p. or decomposition point is recorded.

Treated with alkyl Grignard reagents by the method of Grüttner and Krause (*Ber.*, 1916, **49**, 1546), di-*n*-butyl-lead dichloride yields mixed tetra-alkyl-leads of the type $R_2PbR'_2$. The following compounds were so prepared, the yields given being from 20 g. of di-*n*-butyl-lead dichloride. *Dimethyldi*-n-*butyl-lead* (Found : C, 33·8; H, 6·8; Pb, 58·7. $C_{10}H_{24}Pb$ requires C, 34·2; H, 6·8; Pb, 59·0%), yield 10 g., b. p. 96·5°/5 mm., 108°/10 mm.; *diethyldi*-n-*butyl-lead* (Found : C, 38·0; H, 7·4; Pb, 54·6. $C_{12}H_{28}Pb$ requires C, 38·0; H, 7·4; Pb, 54·6%), yield 14 g., b. p. 90°/1 mm.; *di-n-propyldi*-n-*butyl-lead* (Found : C, 41·1; H, 7·9; Pb, 50·9. $C_{14}H_{32}Pb$ requires C, 41·2; H, 7·9; Pb, 50·9%), yield 17 g., b. p. 120°/1 mm.; *tetra*-n-*butyl-lead* (Found : Pb, 47·2. Calc. for $C_{16}H_{36}Pb$: Pb, 47·6%), prepared previously by Danzer (*loc. cit.*), was obtained in the present work from di-*n*-butyl-lead dichloride and *n*-butylmagnesium bromide, yield 17 g., b. p. 140°/1 mm., 157°/5 mm. (some decomp.) (Danzer gives b. p. 156°/10 mm. in carbon dioxide, which does not accord with our observation) ; *di-n-butyldiisobutyl-lead* (Found : C, 44·0; H, 8·2; Pb, 47·1. $C_{16}H_{36}Pb$ requires C, 44·1; H, 8·3; Pb, 47·6%), yield 13 g., b. p. 135°/1 mm.; *di-n-butyldiisoamyl-lead* (Found : C, 46·4; H, 8·6; Pb, 44·4. $C_{18}H_{40}Pb$ requires C, 46·6; H, 8·7; Pb, 44·7%), yield 20 g., b. p. 135°/0·5 mm.; *di-n-butyldi-dl-amyl-lead* (Found : C, 46·5; H, 8·5; Pb, 44·6%), yield 20 g., b. p. 135°/0·5 mm.

Di-n-*amyl-lead dichloride* (Found : Cl, 16·7; Pb, 48·9. $C_{10}H_{22}Cl_2Pb$ requires Cl, 16·9; Pb, 49·3%), obtained similarly to the corresponding *n*-butyl compound, crystallises from alcohol in thin, glistening, white plates, decomp. 123—125°, turning yellow. The solid decomposes in contact with hot solvents, forming lead chloride. *Di*-n-*amyl-lead dibromide* (Found : Pb, 41·1. $C_{10}H_{22}Br_2Pb$ requires Pb, 40·8%) was prepared similarly to the dichloride by the addition of bromine to an ether–alcohol solution of tri- and tetra-*n*-amyl-leads at −10° until a permanent red colour was developed. The dibromide, which separated out, recrystallised from alcohol as glistening, pale yellow plates, which sintered at 89°. On long standing, and also in contact with hot solvents, the dibromide undergoes partial decomposition to form lead bromide. An alcoholic solution of di-*n*-amyl-lead dibromide gives a yellow precipitate of lead iodide with aqueous potassium iodide. Attempts to prepare di-*n*-amyl-lead di-iodide were unsuccessful, an unstable iodide being obtained that readily decomposed, setting free iodine and lead iodide. *Di*-n-*amyl-lead sulphate* (Found : Pb, 46·1; $C_{10}H_{22}O_4SPb$ requires Pb, 46·6%) was obtained as a fine, white, insoluble powder by neutralising di-*n*-amyl-lead dihydroxide in alcoholic solution with sulphuric acid. The solid sinters at 177°, but remains white.

The following tetra-alkyl-leads were obtained by treating di-*n*-amyl-lead dichloride with alkyl Grignard reagents. *Dimethyldi*-n-*amyl-lead* (Found : C, 38·0; H, 7·5; Pb, 54·2. $C_{12}H_{28}Pb$ requires C, 38·0; H, 7·4; Pb, 54·6%), yield 16 g., b. p. 113°/4 mm., 121°/5 mm., 135°/10 mm.; *diethyldi*-n-*amyl-lead* (Found : C, 41·2; H, 7·9; Pb, 50·7. $C_{14}H_{32}Pb$ requires C, 41·2; H, 7·9; Pb, 50·9%), yield 10 g. from 20 g. of di-*n*-amyl-lead dibromide, b. p. 116—118°/0·5 mm., 157—158°/10 mm. (decomp.) ; *di-n-propyldi*-n-*amyl-lead* (Found : C, 43·9; H, 8·3; Pb, 47·2. $C_{16}H_{36}Pb$ requires C, 44·1; H, 8·3; Pb, 47·6%), yield 17 g., b. p. 150°/1 mm.— when heated towards its b. p. under 10 mm., the liquid decomposes completely with separation of lead; *di-n-butyldi*-n-*amyl-lead* (Found : C, 46·6; H, 8·6; Pb, 44·4. $C_{18}H_{40}Pb$ requires C, 46·6; H, 8·7; Pb, 44·7%), yield 12 g., b. p. 170°/1 mm.; *diisobutyldi*-n-*amyl-lead* (Found : C, 46·7; H, 8·6; Pb, 44·2%), yield 16 g., b. p. 140°/0·5 mm.; *tetra*-n-*amyl-lead* (Found : C, 48·8; H, 9·0; Pb, 41·7. $C_{20}H_{44}Pb$ requires C, 48·8; H, 9·0; Pb, 42·2%), yield 20 g., b. p. 170°/1 mm.; *di-n-amyldiisoamyl-lead* (Found : C, 48·8; H, 9·0; Pb, 41·8%), yield 16 g., b. p. 160°/0·5 mm.; *di-n-amyldi-dl-amyl-lead* (Found : C, 48·9; H, 9·0; Pb, 42·2%), yield 18 g., b. p. 160°/1 mm.; *di-n-amyldi-n-hexyl-lead* (Found : Pb, 39·6. $C_{22}H_{48}Pb$ requires Pb, 39·9%), yield 10 g., b. p. 180°/0·5 mm., $d_4^{20°}$ 1·153.

Di-dl-amyl-lead dichloride (Found : Cl, 17·0; Pb, 49·5. $C_{10}H_{22}Cl_2Pb$ requires Cl, 16·9; Pb, 49·3%) was prepared similarly to the corresponding *n*-butyl compound; from alcohol it separates as pale yellow plates, which partly melt at 67° and decompose very readily, giving lead chloride.

Tetra-dl-*amyl-lead* (Found : Pb, 42·0. $C_{20}H_{44}Pb$ requires Pb, 42·2%), b. p. 150°/0·5 mm.,

was obtained in poor yield by the distillation of a mixture of tetra- and tri-*dl*-amyl-leads prepared by the method of Grüttner and Krause (*loc. cit.*).

When dimethyldi-*n*-amyl lead is stirred with concentrated hydrochloric acid at 35°, very little reaction occurs, but the addition of a small quantity of finely powdered silica gel initiates action, and after 3 hours the whole of the lead alkyl has dissolved, the solid product floating on the excess of acid. Treatment of the product with alcohol effects separation of its constituents, lead chloride, di-*n*-amyl-lead dichloride, and *methyldi*-n-*amyl-lead chloride* (Found : Pb, 51·3. $C_{11}H_{25}ClPb$ requires Pb, 51·8%), short, fine, white needles which sinter at 121—122°, and turn yellow (decomp.).

Calingaërt (*Chem. Rev.*, 1926, **2**, 50) states that when a simple tetra-alkyl-lead is boiled with concentrated nitric acid, lead nitrate is formed. On the other hand, according to Polis (*Ber.*, 1887, **20**, 716, 3331), tetra-aryl-leads when treated with nitric acid give rise to aryl-lead nitrates, $Ar_3Pb(NO_3)_2,xH_2O$. This reaction has been examined in the present work, with a view to ascertain the nature of the primary products. It has been found that when cold concentrated nitric acid is added to a tetra-alkyl-lead, the reaction that follows takes place very slowly with the formation, in the case of compounds containing alkyl groups higher than ethyl, of a dialkyl-lead dinitrate, $2HNO_3 + PbR_4 = R_2Pb(NO_3)_2 + 2RH$. The product floats on the excess of acid, and, after separation, can be recrystallised from alcohol–ether. The addition of a small amount of finely powdered silica gel to the mixture of nitric acid and tetra-alkyl lead increases the rate of interaction, and then bubbles of paraffin rise at a visible speed, but the reaction is still slow. However, a violent reaction ensues on the addition of 1—2 c.c. of ether, and dense fumes of nitrogen oxides are evolved; with most of the alkyl compounds there is also an immediate precipitation of a solid, and in all cases, on cooling, the dinitrate separates.

The reaction was carried out as follows : 2—3 g. of the tetra-alkyl-lead were weighed into a 100-c.c. round-bottomed, long-necked flask fixed in an inclined position, 2 c.c. of ether were then added, and the mixture was well shaken. An excess of nitric acid (*d* 1·42, 10—15 c.c.) was next added, and, after the initial violent reaction had subsided, the mixture was cooled by means of running water. The white solid was filtered off, washed with ether to remove any mononitrate that might have been formed, and then recrystallised from alcohol–ether. An alternative procedure, adopted in certain cases, consisted in evaporating the mixture of nitric acid and organo-lead nitrate in a vacuum desiccator, washing the residue with ether, and recrystallising from alcohol–ether. *Di*-n-*butyl-lead dinitrate* crystallises with 2 mols. of water [Found : Pb, 43·0; H_2O, 7·9. $(C_4H_9)_2Pb(NO_3)_2,2H_2O$ requires Pb, 43·0; H_2O, 7·5%], yield 1·9 g. from 2 g. of tetra-*n*-butyl-lead. The salt separates from alcohol–ether as transparent, hexagonal prisms, which sinter at 116—117°. On standing over phosphoric oxide in a desiccator, the hydrated solid slowly loses water, and forms a white powder of the dehydrated salt, which melts to a milky liquid at 123·5°. Dehydration is quantitative at 40° after 12 hrs. in a vacuum with phosphoric oxide. *Di*-n-*amyl-lead dinitrate dihydrate* [Found : Pb, 40·7; H_2O, 7·1. $(C_5H_{11})_2Pb(NO_3)_2,2H_2O$ requires Pb, 40·7; H_2O, 7·1%] forms hexagonal plates from alcohol–ether, which sinter at 96—98°; yield 0·75 g. from 1·5 g. of tetra-*n*-amyl-lead. Dehydration gives *di*-n-*amyl-lead dinitrate* (Found : Pb, 43·8. $C_{10}H_{22}O_6N_2Pb$ requires Pb, 43·8%). These two alkyl-lead nitrates were also prepared in quantitative yield by treating the corresponding dialkyl-lead dihydroxide in alcohol with nitric acid, and evaporating to the point of crystallisation. *Di*-n-*propyl-lead dinitrate dihydrate* [Found : Pb, 45·8; H_2O, 7·9. $(C_3H_7)_2Pb(NO_3)_2,2H_2O$ requires Pb, 45·7; H_2O, 7·9%] also was obtained in this way; it forms thin plates, m. p. 87—89°.

The only product that could be isolated after tetra-ethyl-lead had been treated with nitric acid was lead nitrate, indicating the relative instability of diethyl-lead dinitrate.

The action of concentrated nitric acid on mixed tetra-alkyl-leads of the type $R_2PbR'_2$ yielded dialkyl-lead dinitrates, together with, in some cases, a small quantity of lead nitrate. A yield of 1·2 g. of di-*n*-amyl-lead dinitrate was obtained from 1·6 g. of dimethyldi-*n*-amyl-lead on treatment with excess of concentrated nitric acid in presence of ether. This reaction is similar to that of hydrochloric acid on tetra-aryl-leads (Gilman, *Rec. trav. chim.*, 1932, **51**, 1054; *J. Amer. Chem. Soc.*, 1933, **55**, 4689), the methyl groups being split off in preference to the *n*-amyl radicals; this is in accordance with the order of electronegativity of radicals given by Kharasch (*J. Amer. Chem. Soc.*, 1932, **54**, 686). Dimethyldi-*n*-butyl-lead (0·9 g.) when treated with nitric acid gave di-*n*-butyl-lead dinitrate (0·8 g.). Diethyldi-*n*-butyl-lead on similar treatment gave di-*n*-butyl-lead dinitrate, which was isolated and identified, together with some lead nitrate and an organo-lead nitrate that could not be identified. All the other di-*n*-butyldialkyl-leads described in the present communication gave, with nitric acid, mixtures that could not be resolved.

In the analysis of the tetra-alkyl-leads and of their bromo-derivatives here described, the lead was determined by dissolving or suspending the compound in carbon tetrachloride, adding a large excess of a 10% solution of bromine in the same solvent, evaporating the resulting mixture nearly to dryness, then adding a small quantity of absolute alcohol, boiling, cooling in ice, and collecting and weighing the lead bromide. In the organo-lead chlorides, nitrates, and sulphates, the percentage of lead was found by first heating the compound with a mixture of concentrated sulphuric and fuming nitric acids, then heating the mixture more strongly until colourless to expel nitric acid, cooling, diluting with water, and precipitating lead sulphate by the addition of alcohol.

Cadmium Dialkyls.—Some of the higher alkyl compounds of cadmium were examined in this work, but they were not obtained sufficiently pure to justify the carrying out of physicochemical measurements on them. These substances appreciably decomposed with separation of metallic cadmium on being kept for only an hour in sealed tubes filled with nitrogen. For the determination of cadmium, such a tube of known tare was immediately weighed and broken under alcohol, excess of 2% sulphuric acid was added, the alcohol was removed by boiling, and the solution was saturated with hydrogen sulphide, the cadmium being precipitated as sulphide, which was collected and weighed.

Di-n-amylcadmium (Found : C, 47·1; H, 8·6; Cd, 44·3. $C_{10}H_{22}Cd$ requires C, 47·1; H, 8·7; Cd, 44·1%) was prepared by refluxing a mixture of 124 g. of anhydrous cadmium chloride with the ethereal solution of *n*-amylmagnesium bromide obtained from 48 g. of magnesium, and then fractionating the product under low pressure. Yield, 16 g., b. p. 105°/2 mm., $d_4^{20°}$ 1·190. *Di-dl-amylcadmium* (Found : C, 47·3; H, 8·6; Cd, 44·2%) was similarly obtained in 8 g. yield, b. p. 94°/2 mm., $d_4^{20°}$ 1·176.

Purification and Measurements.—In addition to the new organo-metallic compounds here described, several others obtained by previous workers have been prepared for the determination of their constants. In every case the substance was finally purified by redistillation under low pressure immediately before the measurements were made on it. Where necessary, due precautions were taken to keep the substance out of contact with the air. The compounds of mercury, tin, and lead used in the measurements were clear, colourless, stable liquids.

Temperature readings were corrected for thermometric errors, and weighings for errors of weights and for buoyancy. Pressures were read by means of standard manometers and barometers. Refractive indices were measured with a Pulfrich refractometer, by Zeiss of Jena, and an Abbé refractometer, by Hilger of London. These instruments were checked at every measurement by the use of water. The measurements of heats of combustion were made with a Berthelot–Mahler bomb calorimeter of the Krocker type, the water equivalent of which had been determined by the combustion of pure benzoic acid, and the thermometer employed had been standardised to 0·01° at the National Physical Laboratory.

Results.—The values of the densities and refractive indices found in the present work are summarised in Table I.

Table II contains the values of the b. p./10 mm., the molecular volumes at 20° ($V_{20°}$), the Lorenz–Lorentz molecular refractivity, $[R_L]$, and the corresponding atomic refractivities $[r_L]$ for the F, D, and C lines. The calculated values of the b. p./10 mm., $t_{10\ mm.}$, are those given by the following equations, which apply to the organo-metallic compounds containing straight carbon chains only (M = molecular weight) :

$$\text{for mercury compounds, } t_{10\ mm.} + 273\cdot1 = 3\cdot378M^{0\cdot3200};$$
$$\text{for tin compounds, } t_{10\ mm.} + 273\cdot1 = 22\cdot566M^{0\cdot1600};$$
$$\text{for lead compounds, } t_{10\ mm.} + 273\cdot1 = 0\cdot867M^{1\cdot037}.$$

It will be noticed that the calculated does not agree with the found value in the case of the methyls. The calculated values of $V_{20°}$ are those given by the following equations, which hold for both *n*- and *iso*-alkyl compounds, *C* denoting the number of carbon atoms in the molecule :

$$\text{for the mercury dialkyls, } V_{20°} = 41\cdot10 + 16\cdot66C;$$
$$\text{for the tin tetra-alkyls, } V_{20°} = 64\cdot35 + 16\cdot55C;$$
$$\text{for the trialkylbromostannanes, } V_{20°} = 75\cdot87 + 16\cdot55C;$$
$$\text{for the lead tetra-alkyls, } V_{20°} = 66\cdot10 + 16\cdot55C.$$

The values of $[r_L]$ have been calculated by deducting the values for carbon, hydrogen, and bromine, given by Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 585). For the purpose of comparisons there have been included some of the results of previous workers (Grüttner, Krause, and Wiernik, *Ber.*, 1917, **50**, 1549; Grüttner and Krause, *ibid.*, p. 1802; *Annalen*, 1918, **415**, 338; Marvel and

TABLE I.

Substance.	$d_4^{20°}$.	$n_F^{20°}$.	$n_D^{20°}$.	$n_C^{20°}$.
Mercury dialkyls.				
Di-*n*-propyl	2·0208	1·5271	1·5170	1·5128
Di*iso*propyl	2·0024	1·5373	1·5263	1·5218
Di-*n*-butyl	1·7779	1·5152	1·5057	1·5018
Di*iso*butyl	1·7678	1·5057	1·4965	1·4927
Di-*n*-amyl	1·6369	1·5087	1·4998	1·4962
Di*iso*amyl	1·6397	1·5074	1·4989	1·4954
Di-*dl*-amyl	1·6700	1·5103	1·5014	1·4977
Di-*n*-hexyl	1·5361	1·5054	1·4973	1·4939
Tin tetra-alkyls.				
Tetra-*n*-butyl	1·0572	1·4802	1·4730	1·4700
Tetra-*n*-amyl	1·0206	1·4796	1·4720	1·4688
Tetra-*dl*-amyl	1·0222	1·4796	1·4730	1·4703
Tetra-*n*-hexyl	0·9959	1·4776	1·4706	1·4677
Tetra-*n*-heptyl	0·9748	1·4765	1·4698	1·4670
Tetra-*n*-octyl	0·9605	1·4756	1·4691	1·4664
Methyltri-*n*-butyl	1·0898	1·4810	1·4735	1·4704
Ethyltri-*n*-butyl	1·0783	1·4806	1·4732	1·4699
n-Propyltri-*n*-amyl	1·0368	1·4806	1·4732	1·4702
Tin bromides.				
Tri-*n*-butyl bromide	1·3365	1·5089	1·5000	1·4964
Tri-*n*-amyl bromide	1·2678	1·5049	1·4963	1·4927
Lead tetra-alkyls.				
Tetraethyl	1·6524	1·5318	1·5195	1·5144
Tetra-*n*-butyl	1·3233	1·5121	1·5119	1·4977
Tetra-*n*-amyl	1·2457	1·5058	1·4966	1·4928
Tetra-*dl*-amyl	1·2346	1·5048	1·4957	1·4919
Dimethyldi-*n*-butyl	1·5210	1·5157	1·5049	1·5004
Dimethyldi-*n*-amyl	1·4398	1·5109	1·5009	1·4969
Diethyldi-*n*-butyl	1·4580	1·5203	1·5093	1·5048
Diethyldi-*n*-amyl	1·3856	1·5140	1·5038	1·4996
Di-*n*-propyldi-*n*-butyl	1·3842	1·5166	1·5062	1·5019
Di-*n*-butyldi*iso*butyl	1·3258	1·5123	1·5021	1·4979
Di-*n*-propyldi-*n*-amyl	1·3238	1·5119	1·5019	1·4979
Di-*n*-butyldi-*n*-amyl	1·2825	1·5080	1·4984	1·4945
Di-*n*-butyldi*iso*amyl	1·2798	1·5088	1·4982	1·4953
Di-*n*-butyldi-*dl*-amyl	1·2779	1·5088	1·4993	1·4953
Di*iso*butyldi-*n*-amyl	1·2860	1·5092	1·4994	1·4954
Di-*n*-amyldi*iso*amyl	1·2438	1·5052	1·4959	1·4921
Di-*n*-amyldi-*dl*-amyl	1·2421	1·5015	1·4923	1·4885

Calvery, *J. Amer. Chem. Soc.*, 1923, **45**, 820; Hager and Marvel, *ibid.*, 1926, **48**, 2696; Krause, *Ber.*, 1926, **59**, 935). In cases where these workers have not calculated the values of molecular and atomic refractivities, these quantities are marked with an asterisk in Table II, but where values are given by these investigators they are indicated with a dagger.

It is found that, within the limits of the pressures usual in the distillation of these compounds, the reciprocal of the absolute b. p. is a linear function of the logarithm of the pressure; *e.g.*, for tetraethyl-lead, the equation $t + 273 \cdot 1 = 2960 \cdot 0/(9 \cdot 4262 - \log_{10} p)$ gives for the b. p. *t*°C., under the pressure *p* mm. of mercury, the following values : 78°/10 mm., 83°/13 mm., 90°/19 mm., 152°/290·5 mm., whilst the respective found values are 77°, 83°, 91—92°, and 152°. For tetra-*n*-propyltin, the corresponding equation is $t + 273 \cdot 1 = 3167 \cdot 8/(9 \cdot 2463 - \log_{10} p)$, and that for diethylmercury is $t + 273 \cdot 1 = 2344 \cdot 7/(8 \cdot 3071 - \log_{10} p)$.

By combining the equations of the last paragraph, and by assuming that the ratio of the abs. b. p.'s of two different alkyls of a metal under one pressure is equal to the ratio of the b. p.'s of the two compounds under another pressure, it is possible to calculate the approximate value of the b. p. of any *n*-alkyl-mercury, -lead, or -tin under any pressure. This is a great help to those engaged in the preparation of new compounds of these types. For instance, if the b. p. of dimethyldiethyl-lead under 18 mm. were required, the equation $t_{18\,\text{mm.}} + 273 \cdot 1 = 0 \cdot 867 M^{1 \cdot 037}$ gives its b. p. as 43°/10 mm., whilst the equation $t + 273 \cdot 1 = 2960 \cdot 0/(9 \cdot 4262 - \log_{10} p)$ gives for the b. p.'s of tetraethyl-lead 78°/10 mm. and 89°/18 mm., whence the required value of the b. p. $= -273 \cdot 1 + (43 + 273 \cdot 1)(89 + 273 \cdot 1)/(78 + 273 \cdot 1) = 53°$ C. (Grüttner and Krause, *Ber.*, 1916, **49**, 1546, found 54°).

The approximate equality of the coefficients of *C* in the four given equations for the molecular volume indicates the constancy of the volume of the CH_2 in these liquids. These equations

TABLE II.

Substance.	B. p. /10 mm. Found.	B. p. /10 mm. Calc.	$V_{20°}$. Found.	$V_{20°}$. Calc.	$[R_L]_F$.	$[R_L]_D$.	$[R_L]_C$.	$[r_L]_F$.	$[r_L]_D$.	$[r_L]_C$.
Mercury dialkyls.										
Dimethyl	0°	19°	74·8	74·4	—	23·72†	23·53†	—	12·28†	12·15†
Diethyl	48	48	104·9	107·7	—	33·26†	33·02†	—	12·59†	12·45†
Di-*n*-propyl	73	77	141·9	141·1	43·63	42·93	42·64	13·30	13·02	12·87
Diisopropyl	63	—	143·2	141·1	44·74	43·98	43·66	14·50	14·07	13·90
Di-*n*-butyl	105	105	177·0	174·4	53·41	52·57	52·23	13·83	13·43	13·27
Diisobutyl	86	—	178·1	174·4	52·87	52·06	51·72	13·30	12·91	12·76
Di-*sec.*-butyl	—	—	178·5	174·4	—	53·48*	—	—	14·34*	—
Di-*tert.*-butyl	—	—	180·0	174·4	—	54·80*	—	—	15·65*	—
Di-*n*-amyl	133	132	209·4	207·7	62·49	61·57	61·19	13·58	13·19	13·04
Diisoamyl	125	—	209·1	207·7	62·25	61·37	61·00	13·34	12·99	12·85
Di-*dl*-amyl	—	—	205·4	207·7	61·42	60·51	60·13	12·51	12·13	11·98
Di-*tert.*-amyl	—	—	207·9	207·7	—	—	—	—	—	—
Di-*n*-hexyl	158	159	241·4	241·0	71·65	70·67	70·26	13·40	13·06	12·91
Tin tetra-alkyls.										
Tetraethyl	73	73	195·9	196·8	55·75*	54·90*	54·56*	13·95*	13·56*	13·42*
Tetra-*n*-propyl	112	112	262·9	263·0	75·03*	73·95*	73·52*	14·56*	14·13*	13·99*
Tetra-*n*-butyl	145	147	328·2	329·2	93·27	92·07	91·57	14·12	13·78	13·65
Tetra-*n*-amyl	181	180	394·9	395·5	112·10	110·64	109·99	14·28	13·88	13·63
Tetra-*dl*-amyl	174	—	394·3	395·5	111·93	110·60	110·00	14·11	13·84	13·69
Tetra-*n*-hexyl	209	210	461·1	461·6	130·40	128·78	128·10	13·91	13·55	13·40
Tetra-*n*-heptyl	239	239	528·5	527·8	149·20	147·40	146·74	14·04	13·70	13·66
Tetra-*n*-octyl	268	266	594·8	594·1	167·62	165·66	164·84	13·78	13·48	13·37
Triethyl-*n*-propyl	77	83	213·8	213·3	60·86*	59·95*	59·58*	14·39*	13·99*	13·85*
Triethyl*iso*butyl	86	—	230·8	229·9	65·72*	64·76*	64·37*	14·58*	14·18*	14·03*
Methyltri-*n*-propyl	93	93	230·5	229·9	—	—	—	—	—	—
Triethyl*iso*amyl	—	—	247·5	246·4	70·28*	69·27*	68·86*	14·47*	14·07*	13·92*
Ethyltri-*n*-propyl	101	102	246·1	246·4	70·33*	69·30*	68·89*	14·52*	14·10*	13·95*
Triethyl-*n*-amyl	102	102	246·0	246·4	70·15*	69·13*	68·72*	14·34*	13·93*	13·78*
Methyltri-*n*-butyl	121	121	279·8	279·5	79·66	78·61	78·15	14·52	14·17	14·02
Tri-*n*-propyl-*n*-butyl	121	121	279·6	279·5	—	—	—	—	—	—
Ethyltri*iso*butyl	115	—	295·9	296·1	84·31*	83·12*	82·64*	14·50*	14·06*	13·91*
Ethyltri-*n*-butyl	129	130	295·8	296·1	84·11	82·97	82·50	14·30	13·91	13·77
n-Propyltri-*n*-amyl	163	164	361·7	362·3	102·87	101·51	100·95	14·39	13·99	13·84
Tin bromides.										
Tri-*n*-butyl	—	—	276·7	274·5	82·62	81·39	80·90	14·26	13·81	13·66
Tri-*n*-amyl	—	—	324·9	324·1	96·37	94·98	94·39	14·00	13·54	13·36
Diethyl*iso*butyl	—	—	207·7	208·3	63·76*	62·72*	62·32*	14·07*	13·61*	13·47*
Diethyl dibromide	—	—	—	—	53·36*	52·30*	51·91*	14·46*	13·90*	13·73*
Tin tetrabromide	—	—	130·4	—	49·91*	48·60*	48·10*	13·91*	13·14*	12·89*
Lead tetra-alkyls.										
Tetramethyl	6	12	134·0	132·3	—	40·18†	39·83†	—	17·31†	17·07†
Tetraethyl	78	74	195·7	198·5	60·62	59·45	58·96	18·82	18·10	17·81
Tetra-*n*-propyl	—	—	260·0*	264·7	—	78·60†	78·03†	—	18·78†	18·49†
Tetra*iso*propyl	—	—	258·6*	264·7	—	79·87†	79·24†	—	20·05†	19·70†
Tetra-*n*-butyl	—	—	329·9	330·9	98·77	97·11	96·42	19·63	18·82	18·50
Tetra-*n*-amyl	—	—	394·6	397·1	117·20	115·39	114·64	19·38	18·63	18·34
Tetra-*dl*-amyl	—	—	398·2	397·1	118·05	116·25	115·49	20·23	19·49	19·19
Tetra*iso*amyl	—	—	398·4	397·1	—	116·13†	115·37†	—	19·37†	19·05†
Trimethylethyl	27	27	149·5	148·9	—	45·07†	44·68†	—	17·58†	17·33†
Trimethyl-*n*-propyl	39	43	167·2	165·4	—	49·95†	49·53†	—	17·84†	17·57†
Methyltriethyl	60	59	180·7	182·0	—	54·70†	54·25†	—	17·97†	17·70†
Trimethyl-*n*-butyl	58	59	184·4	182·0	—	54·63†	54·20†	—	17·90†	17·65†
Dimethylethyl-*n*-propyl	56	59	182·4	182·0	—	54·66†	54·26†	—	17·93†	17·71†
Dimethyldi-*n*-propyl	72	74	198·8	198·5	—	59·28†	58·81†	—	17·94†	17·66†
Methyldiethyl-*n*-propyl	72	74	197·0	198·5	—	59·34†	58·87†	—	18·00†	17·72†
Triethyl-*n*-propyl	93	90	212·4	215·1	—	64·19†	63·69†	—	18·23†	17·94†
Methyltri-*n*-propyl	100	105	230·6	231·6	—	68·93†	68·41†	—	18·35†	18·06†
Dimethyldi-*n*-butyl	108	105	231·0	231·6	69·75	68·52	68·00	18·61	17·94	17·66
Diethyldi-*n*-propyl	99	105	229·3	231·6	—	69·04†	68·52†	—	18·46†	18·19†
Ethyltri-*n*-propyl	111	121	246·0	248·2	—	73·77†	73·23†	—	18·57†	18·29†
Dimethyldi-*n*-amyl	135	137	263·5	264·7	78·94	77·63	77·10	18·46	17·82	17·57
Diethyldi-*n*-butyl	—	—	260·3	264·7	79·16	77·75	77·16	18·68	17·93	17·63
Diethyldi-*n*-amyl	—	—	294·1	297·8	88·53	87·05	86·43	18·73	18·00	17·71
Di-*n*-propyldi-*n*-butyl	—	—	294·4	297·8	89·00	87·49	86·86	19·19	18·43	18·13
Di-*n*-butyldi*iso*butyl	—	—	328·5	330·9	98·62	96·96	96·27	19·47	18·67	18·35
Di-*n*-propyldi-*n*-amyl	—	—	329·0	330·9	98·70	97·07	96·41	19·56	18·78	18·49
Di*iso*butyldi-*n*-amyl	—	—	360·0	364·0	107·66	105·91	105·18	19·18	18·38	18·07
Di-*n*-butyldi-*n*-amyl	—	—	361·4	364·0	107·74	106·01	105·31	19·27	18·49	18·20
Di-*n*-butyldi*iso*amyl	—	—	362·0	364·0	108·11	106·20	105·68	19·64	18·68	18·56
Di-*n*-butyldi-*dl*-amyl	—	—	362·7	364·0	108·27	106·56	105·83	19·79	19·03	18·72
Di-*n*-amyldi-*dl*-amyl	—	—	395·8	397·1	116·69	114·88	114·12	18·87	18·12	17·81
Di-*n*-amyldi*iso*amyl	—	—	395·2	397·1	117·26	115·43	114·68	19·44	18·67	18·38

permit the calculation of densities; *e.g.*, for ethyltri-*n*-propyltin, $d_4^{20°}$, calc., 1·124 (found, 1·123); for diethyldi-*n*-propyl-lead, $d_4^{20°}$, calc., 1·517 (found, 1·532).

It will be seen from Table II that, in general, the atomic refractivity in the *n*-alkyl derivatives of mercury and of lead increases slightly with increase of molecular weight up to the butyl member. However, the increment falls off as the series is further ascended (cf. Tiffeneau and Sommaire, *Bull. Soc. chim.*, 1923, **33**, 293), as will be seen from the following table.

Increments, Δ, in atomic refractivity, $[r_L]$.

Metal	Mercury. $[r_L]_D$.	Δ.	Lead. $[r_L]_D$.	Δ.
Methyl	12·28		17·31	
Ethyl	12·59	0·31	18·10	0·79
n-Propyl	13·02	0·43	18·78	0·68
n-Butyl	13·43	0·41	18·82	0·04
n-Amyl	13·19	−0·24	18·63	−0·19
n-Hexyl	13·06	−0·13	—	

The atomic refractivity of mercury is usually the same when the compound contains primary *iso*alkyl groups as it is when corresponding *n*-alkyl groups are present, and this applies also for the atomic refractivities of lead in the corresponding compounds, but there is a definite exaltation when *sec.*-alkyl groups are present, *e.g.*, di-*n*-propylmercury, $[r_L]_D$, 13·02; di*iso*propylmercury, $[r_L]_D$, 14·07; di-*n*-butylmercury, $[r_L]_D$, 13·43; di-*sec.*-butylmercury, $[r_L]_D$, 14·34; tetra-*n*-propyl-lead, $[r_L]_D$, 18·78; tetra*iso*propyl-lead, $[r_L]_D$, 20·05. The effect is still more marked with *tert.*-alkyl groups, *e.g.*, di-*tert.*-butylmercury, $[r_L]_D$, 15·65.

The mean values of the atomic refractivities of mercury, tin, and lead, when attached to primary alkyl groups, calculated from the data of Table II, are given below :

Atomic refractivities.

	F.	D.	C.
Mercury	13·34	12·84	12·70
Tin	14·26	13·87	13·72
Lead	19·24	18·33	18·05

Table III summarises the results obtained in the thermal measurements, and also includes the values given by Berthelot (*Compt. rend.*, 1899, **129**, 918), which are asterisked. On combustion in the bomb calorimeter, the alkyl derivatives of mercury left the metal, and those of tin, stannic oxide. The values of the heats of combustion assumed in calculating the heats of formation are as follows : diamond, 94 kg.-cals.; hydrogen, 34·5; tin, 138.

TABLE III.

	Heat of combustion, kg.-cals. per g.-mol.	Heat of formation, kg.-cals. per g.-mol.		Heat of combustion, kg.-cals. per g.-mol.	Heat of formation, kg.-cals. per g.-mol.
Dimethylmercury	431 *	−36	Di*iso*amylmercury	1653	+ 46
Diethylmercury	734 *	−13	Tetraethyltin	1521	+ 59
Di-*n*-propylmercury	1036	+11	Tetra-*n*-propyltin	2163	+ 69
Di*iso*propylmercury	1050	− 3	Tetra-*n*-butyltin	2773	+111
Di-*n*-butylmercury	1342	+31	Tetra-*n*-amyltin	3384	+152
Di*iso*butylmercury	1341	+32			

It will be observed that in both *n*-alkyl series the heat of formation shows a regular trend with increasing molecular weight.

The considerable difference between the heats of formation of *iso*- and *n*-propylmercury, *i.e.*, between those of a secondary and a primary alkyl compound, is reminiscent of the difference between the molecular refractivities of these compounds, which has already been discussed, whilst the equality of the heats in the cases of the mercury compounds of *iso*- and *n*-butyl, both primary groups, is paralleled by the general closeness of the refractivities of *n*- and corresponding primary *iso*-alkyl compounds.

Chemical Problems in Crop Production.

By SIR EDWARD JOHN RUSSELL, O.B.E., D.Sc., F.R.S.

THE classic chemical problems in crop production centre round the feeding of plants. It was in 1840 that Liebig by chemical reasoning and Lawes by empirical trials applied in practice the knowledge gained by plant physiologists about the nutrition of plants. Up to that time many agriculturists, knowing nothing about the scientific evidence to the contrary, had assumed that plants feed on the organic matter in the soil. Liebig in his vigorous writings showed them that this was not so; he pieced together the scientific knowledge and gave a convincing picture of the plant deriving most of its food from the air in the form of carbon dioxide and oxygen, and the remainder from the soil : water, and simple compounds of nitrogen, phosphorus, sulphur, potassium, calcium, magnesium, iron and other elements. These are then built up into the complex carbohydrates, proteins and other substances which finally form the plant tissues. Liebig argued that the soil resources could be increased by the addition of the appropriate chemical compounds, and Lawes showed how to do it; he set up experimental fields at Rothamsted and a factory in London, thus starting the artificial fertiliser industry which has now grown to such enormous dimensions that some 35 or 40 million tons are made annually in the different countries of the world. There are many technical problems connected with the industry that could profitably be discussed, but I shall confine myself to those relating to the agricultural side. For many years these were mainly concerned with showing how to fit the fertilisers into everyday farm use. The results were very striking.

Crop increases of 30 or 50% were not uncommon : the cereal crops were greatly increased by nitrogenous manures, and the very important root crops by superphosphate; the Rothamsted field plots started in 1843 afforded such striking demonstrations as farmers had never before seen. In the words of Gilbert, the distinguished collaborator of Lawes, the unmanured crops growing alongside of their neighbours might almost be fancied to say : " If you won't feed me I won't grow." Those were spacious days for the farmer; prices were high and costs low; there was no need for stinginess in applying fertilisers. They were put on the ground in adequate amounts and a good response fully repaid the cost.

As years went by, costs began to rise and prices to fall; the margin of profit became exceedingly narrow and finally disappeared. New and more economical methods were required and the chemist was called in to find how little of the various fertilisers needed to be added to soils to serve for a particular crop. The first hypothesis had been that plants took from the soil those things they needed, and if, therefore, one wished to discover the fertiliser requirements of plants it was only necessary to find out what quantities of fertiliser constituents the plant contained. Average crops were therefore analysed so as to discover the amounts of phosphorus, potassium, nitrogen, etc., present; the soils also were analysed to find the amounts per acre of these elements present in suitable form for plant nutrition, and a simple subtraction sum showed how much, if any, artificial fertiliser need be supplied. The method was much used some 30 or 40 years ago : it was highly developed in the United States by Cyril Hopkins, who spoke of drawing up the " Invoice of the Soil " :

Phosphate in crop	.	.	.	30 lb. per acre.
„ „ soil	.	.	.	600 „ „ „
Average of good soils in district		2000 „ „ „

There seems sufficient phosphate for a number of crops, but, as the amount is far below the average content, there will certainly be need for phosphatic fertiliser if the average soils are known to respond—which in the region in question they were. This procedure was simple; it had, however, the weakness that it was not adequate—for two reasons :

(1) one cannot say exactly how much available plant food there is in the soil; and (2) the plant is not a fixed definite entity, it has considerable range of variation.

It might seem relatively easy to determine how much phosphate or potash a given soil contains, but actually the total values given by ultimate analysis have had only limited utility. Hopkins was able to get something out of them, as also was Prescott in Australia, but in normal English experience they are not helpful. Better results have been obtained by adopting some analytical method that distinguishes between the more and the less soluble constituents—a distinction first emphasised by Daubeny in 1845 and reduced to laboratory terms by Dyer in 1894 : indeed Dyer's method still remains the most useful we have.

The amounts of nutrient and other materials in the plant, however, are not determined by the needs of the plant but by the quantities available. The plant roots act like a partially permeable membrane; they absorb some of everything that is soluble in the soil; not, however, in the proportion in which it exists in the soil, but in a proportion modified by certain characters of the plant. This is well illustrated by the following figures showing the mineral constituents of grasses and clovers growing intermingled on the Rothamsted grass plots :

Variation in Composition of Mineral Matter in Plants growing side by side (Rothamsted—Park Grass).

	% in pure ash.			% in pure ash.	
	Grasses.	Legumes.		Grasses.	Legumes.
CaO	7·6—11·8	21·4—30·3	P_2O_5	5·7— 9·7	5·1—8·6
MgO	2·4— 3·7	3·6— 7·5	SiO_2	17·3—36·6	1·3—1·9
K_2O	22·6—37·9	11·2—31·3			
Na_2O	0·4— 5·3	0·6— 9·6			

Some of these absorbed substances greatly stimulate the production of carbohydrates and proteins in the plant : others do not. The final composition of the plant is therefore profoundly affected by the composition of the soil, and, except in cases of extreme deficiencies, is not a good index of the fertiliser requirements of the plant.

A different approach has therefore become necessary. It is recognised that the subject is much more complex than had been supposed and it has had to be put on a much broader basis. The purpose of modern work is to discover the factors that govern the the growth and composition of plants, and having done that, to find the simplest and most economical method of bringing them under control. The study of soil fertility thus resolves itself into two parallel sets of investigations. Plant physiological work shows what the plant needs in order to attain its maximum growth : more precisely, how growth is affected by variations in the conditions, especially in the supplies of nutrients, water and air for the root, reaction of the medium, etc. Studies by soil investigators show how far a particular soil is likely to satisfy the conditions for full plant growth, and how it can be made to do so better than it naturally would. Soil fertility is dependent on five main factors :

Adequate plant food supplies. Adequate water supply. Air supply to the roots. Adequate space for the root system. Absence of injurious substances.

In practice these are closely linked. A food supply adequate for one level of water supply is quite inadequate for another. F. G. Gregory and F. Crowther made some good experiments in the Sudan showing that, as the amount of irrigation water increased, the response to added nitrogen fertiliser also increased. It is therefore impossible to speak of the adequacy of the soil supplies of plant food except in terms of water supply. The same holds true of the other conditions of growth, particularly of air supply, which is largely a matter of soil texture.

The relation between the quantity of nitrate in the soil and the quantity of nitrogen present in the plant is fairly simple. The total quantity of nitrogen in the crop is roughly proportional to the supply, but the way in which the nitrogen is used varies according

to the amount present and the water supply. The added nitrogen can lead to a corresponding increase in crop without particular change in nitrogen content, or if for any reason it fails to increase the yield it can cause an increase in nitrogen content that may become very marked.

Extreme cases being omitted, the variations in composition due to increases in nitrogen supply are much less than the increases in yield. The first increments of nitrogen give considerable increments of crop: later ones give less. So the percentage of nitrogen in the crop, and especially in the grain, is first unchanged or even falls as the nitrogen supply increases, but with later increments of nitrogen it rises steeply. Over a fairly wide range the nitrogen content is more affected by the water supply than by the nitrogen supply. This is what happens in normal fertility conditions; it holds not only for nitrogen but for the other elements that increase plant growth: the fertiliser causes the plant to grow more but does not much affect its composition or its quality.

Thus sulphate of ammonia in conjunction with superphosphate and potassic fertilisers usually increases the potato crop by some 15 to 20 cwts. per acre for each cwt. that is given up to 2, 3, or sometimes 4 cwt. per acre. The change in composition is only slight, as also is the change in marks assigned by an expert chef for quality. On the other hand the effect of soil differences is very great, as shown by a comparison of the Rothamsted with the Woburn results :

Marks for Quality of Steamed Potatoes (1929).

Cwts. K₂O per acre.	Woburn (light soil).	Rothamsted (heavy soil).	Cwts. N per acre.	Woburn (light soil).	Rothamsted (heavy soil).
0	32·6	28·5	0	34·4	29·2
0·5	33·6	29·5	0·3	33·3	29·3
1·0	34·5	29·6	0·6	32·9	29·1

Percentage of Dry Matter in Tubers grown with Different Potassic Fertilisers.

	No potassic fertiliser.	Sulphate of potash.	Muriate of potash.	"30% Potash salt."	Rate of dressing, cwt. K₂O per acre.
Woburn, 1929	27·5	26·7	26·2	24·8	1·0
Rothamsted, 1929	26·1	25·9	24·9	24·2	1·0
,, 1930	23·1	23·3	22·7	22·1	0·8
,, 1931	20·9	20·5	20·2	20·2	0·8
,, 1932	22·6	22·1	—	—	0·8

Remarkable results are obtained when one gets away from the normal fertility range to the extremes of deficiency or excess. The form of the plant changes, in extreme cases considerably; this is well shown in the Rothamsted experiments with mangolds. A large excess of nitrogen and a prolonged deficiency of potassium bring about striking changes in the plant and affect its reaction to insect and fungus attack. Wallace at Long Ashton has shown that nitrogen starvation of apple trees heightens the colour of the fruit.

Although it is not possible to lay down precise fertiliser recipes, crops do show certain general requirements. Practically all crops respond to nitrogenous fertilisers. Root and potato crops frequently respond also to superphosphate, and grass land to basic slag; leguminous crops, mangolds, potatoes and fruit commonly to potassic fertilisers also. Wallace has shown that potassic and nitrogenous fertilisers are as a rule the most important fertiliser elements for fruit, phosphate being advantageous only for cover crops and for strawberries. In the West country at least, the potassium supply is the key to the successful nutrition of fruit trees, and by extending the use of potassic fertilisers it has been possible to extend fruit growing and improve greatly the yields and quality in existing plantations. Trees suffering from shortage of potassium show a curiously high phosphorus content.

Differences in composition of the crop may have far-reaching consequences. Varieties of wheat have been bred at Svalof for resistance to winter frost; successful ones are found (Bengt Lidfores; Åkerman) to contain a higher percentage of sugar in the leaf than the others. It is not supposed that the sugar confers frost resistance : the evidence

is rather that the freezing of water in the intracellular spaces of the leaf causes water to pass out from the cell, making the cell sap more and more concentrated till finally the protein is irreversibly precipitated, apparently by a salting-out process, and the cell then dies. Maximov has shown, however, that the presence of sugar in the sap protects the protein against precipitation.

There are also some unexpected results. The same sugar that is associated with frost resistance also makes the leaves attractive to hares, so that winter resistant varieties tend to be eaten more than others.

The composition of the crop naturally affects its value as food, especially as animal food; this is particularly so for grass, which forms a large part, sometimes indeed the whole, of the food of the animals. In its early stage grass is richer in protein and in mineral matter than at any later period; it therefore has high feeding value and efforts are now being made to preserve dried young grass for winter feeding. Among its other valuable constituents is carotene, the precursor of vitamin-*A* and the cause of the rich yellow colour in cream. Experiments at Jeallots Hill have shown that yellow cream can be obtained in winter if the animal is given some of this dried grass.

In the southern hemisphere, notably Australia and South Africa, and occasionally in England and Scotland, pronounced deficiencies of calcium, phosphorus, or other elements sometimes occur in soil, causing equally pronounced deficiencies in composition of the vegetation, and these lead to marked nutritional troubles with the animals. These were first studied by Arnold Theiler and his colleagues in South Africa and the subject is being developed at the Rowett Institute, Aberdeen. Typical analyses of herbage associated with healthy and with diseased conditions of the animals are as follows :

Percentage of Mineral Constituents in Dry Matter of Herbage.

	Scottish hill pastures.		Kenya.		New South Wales.	
	Healthy.	Diseased.	Healthy.	Diseased.	Healthy.	Diseased.
CaO	0·65	0·21	1·00	0·49	0·465	0·168
P_2O_5	0·67	0·29	0·93	0·19	0·184	0·047
K_2O	2·66	1·51	2·25	0·83	0·143	0·087
Na_2O	0·37	0·12	0·07	0·02	—	—
Cl	0·64	0·52	0·42	0·18	—	—
N	2·50	2·05	—	—	—	—
Total ash	7·18	5·33	—	—	—	—
Silica-free ash	5·85	2·82	—	—	—	—

The remedy consists in supplying the missing elements as " licks " or in fertilisers.

Where the diet includes a number of foods (as the ordinary human diet), differences in composition of individual foods tend to even out, so that for practical purposes the composition of individual items has usually little dietetic significance.

The factor of competition comes into play and introduces complications when several plants are growing together, such as the mixture of leguminous and non-leguminous plants grown for silage or fodder purposes or occurring naturally in grass land. Leguminous plants derive their nitrogen from the bacteria living in the nodules on their roots; these fix nitrogen from the air and make the plants independent of nitrogenous fertiliser. The non-leguminous plants, however, are much favoured by nitrogenous fertiliser, and grow so vigorously that they tend to crowd out the leguminous vegetation. Thus it may happen that additions of nitrogenous fertiliser cause no increase in the amount of protein produced per acre. Phosphates, on the other hand, favour the leguminous plants, so that these increase when phosphatic fertiliser is supplied. This accounts for the remarkable improvements effected by basic slag on pasture land.

In regard to these principal elements of plant nutrition it is now recognised that more and better field experiments are needed to provide the main facts on which the agricultural chemist can then proceed to work. The methods of field experiments have recently been completely overhauled; the experiments of course can never be exact, but they are now done in such a way that each experiment gives a measure of its own error. Simultaneously, chemical examination of the soils is made.

In recent years it has been found that certain elements other than the classical ones are needed in very small amounts. Larger quantities become harmful, but the proper small quantity is indispensable.

Boron has been much studied at Rothamsted. Miss Warington found that it is essential for the proper development of broad beans, and later workers have shown that other plants need it also. Sugar beet affords an interesting example : in absence of the necessary trace of boron a certain disease appears, which has caused some trouble in central Europe and in the Irish Free State.

Manganese has been studied by Samuel and Piper at the Waite Institute, Adelaide. A trace of manganese sulphate (1 part per million) was found to be essential to the growth of plants. In its absence oats become liable to the grey fleck disease.

Allison in Florida has shown that minute traces of copper are essential to plant growth : he has obtained dramatic increases of yield on the Everglade soils by additions of traces of copper sulphate. We have, however, not yet found soils in this country that respond to copper salts. Zinc appears to be essential at any rate for fruit trees : in its absence the curious rosette diseases set in.

Lithium salts are stated by Sir Rowland Biffen to confer resistance to mildew and yellow rust on wheat grown in pots.

Molybdenum salts injected into plants have been found by Miss Sheffield to induce a trailing habit of growth and also to produce symptoms apparently identical with those of virus disease in *Solanum nudiflorum*. W. A. Roach shows that the roots of fruit trees vary in their power of assimilating molybdenum from the soil : some can do it and others cannot.

Some of these curious stimulating substances are organic. They were first called auximones or growth promoters; now they are called auxins or growth enzymes. Owing to the difficulty of working with them it has not always been possible to distinguish their effects from those of the inorganic promoters, and some of the auximone effects of the older workers are probably attributable to iron. But these are cases where the active agent is probably an organic substance, though owing to difficulties of working it is not possible to be quite sure. F. W. Went and Kozl have recently isolated from the growing point of plants an auxin which increases the growth of the upper parts by stimulating the elongation of the cell, and restricts the growth of the roots; they have gone so far as to ascribe the formula $C_{18}H_{32}O_5$ to one form of the auxin and $C_{18}H_{30}O_4$ to another.

A remarkable substance has recently been isolated by H. G. Thornton at Rothamsted. The invasion of the root hairs of leguminous plants by the nitrogen-fixing bacteria is preceded by an excretion from the roots, which causes the bacteria in the soil to multiply. In turn the bacteria excrete something which causes the root hairs to multiply and to curl : on the inner bend of the curl the bacteria enter. This substance has been isolated and is being studied.

The late S. U. Pickering obtained evidence of plant excretions capable of injuring other plants : these results have never yet been satisfactorily explained. There is much empirical knowledge about the harmful effect of growing plants on soil : fruit stocks, for instance, cannot be raised in succession on the same land, but new land is needed for each crop. Whether this is the result of excretions or of exhaustion of some essential minor element is not known.

The growing plant also affects the soil in other ways. Wallace has shown that grass grown as a cover crop raises the potassium and the iron content of the soil water and may thus cure iron and potassium deficiencies on certain soils; it also lowers the N/K ratio. He thus explains the paradoxical result that clean culture of fruit is not always the best : weeds in the orchard have their uses.

The production of cellulose in the plant is now being studied at Rothamsted by A. G. Norman and is opening up considerable possibilities in view of its importance in industry.

The ripened seed has its own group of problems. Barley has been studied most completely and L. J. Bishop has found surprising regularities in the make-up of the grain under various conditions of growth. The nitrogen content may vary from 1·2 to 2·4% and the proteins and carbohydrates change correspondingly, but always in accordance

with a definite pattern which remains constant for any given variety. The value of barley for brewing depends to a considerable extent on the quantity of nitrogen compounds present, large amounts being detrimental, especially for beers that have to be kept for some time before consumption. The value of wheat for baking, on the other hand, is usually enhanced by high protein content, but it is also much affected by the physical state of the protein.

Many of the chemical problems in agriculture are shifting over to the direction of physical chemistry and especially to the branch that deals with colloids.
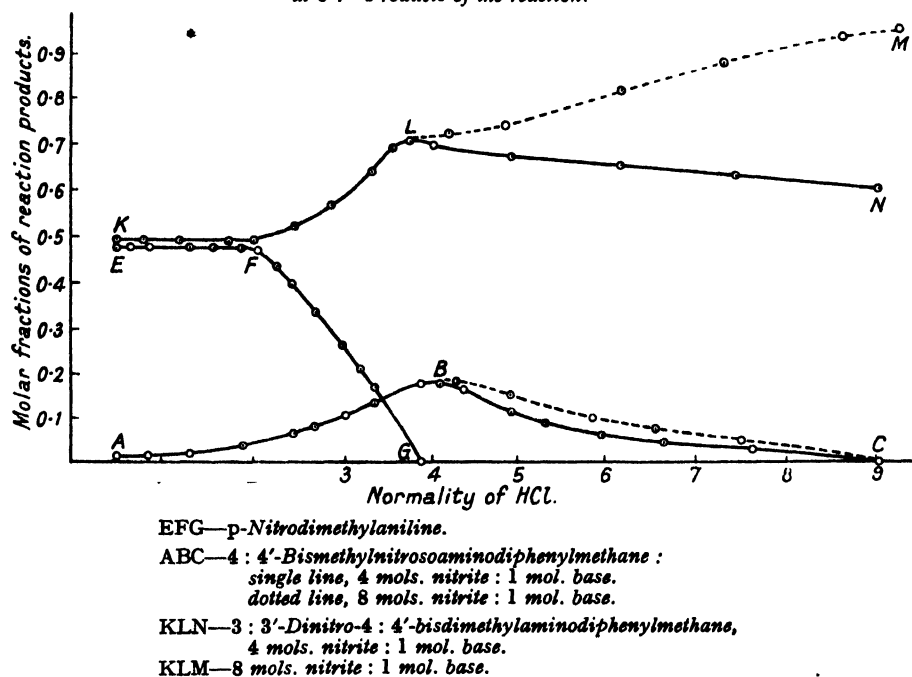
11. *The Action of Nitrous Acid on Tertiary Amines: the Influence of Acidity.*

By CHARLES DONALD and T. HAROLD READE.

THIS communication records the behaviour of Michler's ketone (4 : 4'-bisdimethylaminobenzophenone), Michler's hydride (4 : 4'-bisdimethylaminodiphenylmethane), and the corresponding bisdiethyl base towards aqueous sodium nitrite and hydrochloric acid at various dilutions at 0°.

FIG. 1.

Nitrous acid and 4 : 4'-bisdimethylaminodiphenylmethane in hydrochloric acid of various concentrations at 0°. Products of the reaction.

EFG—p-*Nitrodimethylaniline.*
ABC—4 : 4'-*Bismethylnitrosoaminodiphenylmethane :*
    single line, 4 *mols. nitrite :* 1 *mol. base.*
    dotted line, 8 *mols. nitrite :* 1 *mol. base.*
KLN—3 : 3'-*Dinitro-4 : 4'-bisdimethylaminodiphenylmethane,*
    4 *mols. nitrite :* 1 *mol. base.*
KLM—8 *mols. nitrite :* 1 *mol. base.*

With Michler's hydride, the products isolated by Pinnow (*Ber.,* 1894, **27**, 3867), namely, 3 : 3'-dinitro-4 : 4'-bisdimethylaminodiphenylmethane, 4 : 4'-bismethylnitrosoaminodiphenylmethane, and *p*-nitrodimethylaniline, were again obtained : they represent three types of action, (1) nuclear nitration, (2) nitrosoamine formation by loss of alkyl groups from the nitrogen atoms, and (3) fission (accompanied by nitration), respectively. We find that the type of action which predominates is influenced by the normality of the mineral acid solution, fission being characteristic of low concentrations, nuclear nitration of high, and nitrosoamine formation reaching a true maximum at intermediate concentrations (normality, 3·8), as is shown in Fig. 1, where allowance has been made for 2 mols.

of hydrogen chloride used in dissolving the base, and 4 mols. used in attacking 4 mols. of sodium nitrite. The corresponding bisdiethyl-hydride behaved analogously. Michler's ketone, however, gave only mono- and di-nitrosoamines, the latter reaching a true maximum in 3N-hydrochloric acid (Fig. 2).

The large yields of mononitrosoamine obtained at low concentrations of hydrogen chloride are probably due mainly to its being removed from the sphere of action owing to its low solubility in the dilute acid.

Important theoretical issues arise from these observations. In the first place, the constitution of the amine has an over-riding influence, and Hodgson's generalisation (*J. Soc. Dyers and Colourists*, 1931, April), that positive substituents (which increase the basicity of the amine) favour nuclear nitration whereas negative substituents favour the formation of nitrosoamines, is confirmed; for Michler's ketone is a much weaker base than either of the hydrides investigated. Secondly, the fact that the concentration of external acid has a lesser but nevertheless a decided effect upon the nature of the end products obtained from these hydrides recalls the fact that these two influences—internal substituents and external acidity—are those known to govern the diazonium ⇌ diazo

FIG. 2.

Nitrous acid (4 mols.) and 4 : 4'-bisdimethylaminobenzophenone (1 mol.) in hydrochloric acid of various concentrations at 0°.
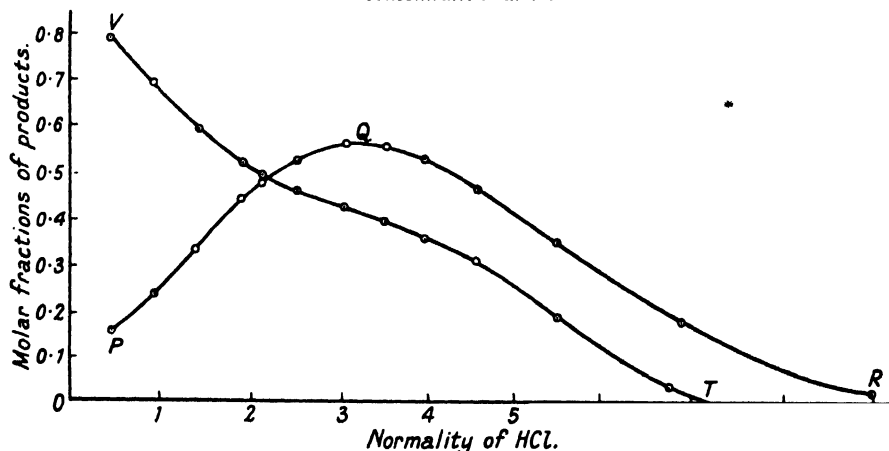

PQR—4 : 4'-Bismethylnitrosoaminobenzophenone.
VT—4-Dimethylamino-4'-methylnitrosoaminobenzophenone.

change, and strongly suggests that an interchange between unstable intermediate compounds analogous to diazonium and diazo-forms plays a part in the reactions of these tertiary amines with nitrous acid also.

The rate of diazotisation of the salts of primary amines is greatly accelerated by increase of the concentration of mineral acid up to 4N (Ueno and Suzuki, *J. Soc. Chem. Ind. Japan*, 1933, **86**, 615B), and if this applies also to the transposition of the salts of tertiary amines into their diazonium analogues, the shapes of the nitrosoamine graphs which show true maxima are qualitatively accounted for, and also that for the nuclear nitration product, provided that a diazonium form is the precursor of nuclear nitration, a diazo-form of nitrosoamine formation; for the production of the latter is hindered by acidity greater than 4N, and yet the diazo-form must be produced from its diazonium analogue whose formation from the aminic salt is favoured by increasing acidity up to 4N *ex hypoth.* The process may be written :

Aminic salt ⟶ diazonium analogue ⇌ diazo-analogue

$\downarrow$ $\downarrow$

nuclear nitration   nitrosoamine
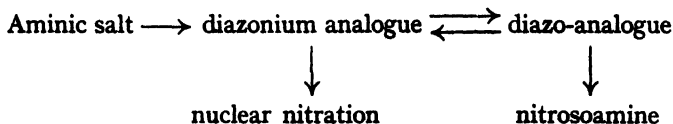
If the nitrite in our experiments at 0° was wholly replaced by sodium nitrate, no action was discernible; hence the usual equations, $3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$ and $RH + HNO_3 \longrightarrow R\cdot NO_2 + H_2O$, employed to represent nitration by (initially) nitrous acid are inadequate. At higher temperatures, however, the nitro-compound was obtained, but neither nitrosoamine nor fission product, when nitrate was used.
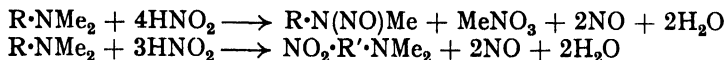
When a portion only of the nitrite was replaced by nitrate at 0°, full yields of the nitration product were obtained with diminished yields of nitrosoamine proportional to the molar fraction of nitrite used. A formulation is given later which takes these observations into account, the final change being akin to a nitroamine transformation into the nuclear nitro-compound.

Fig. 3 shows that in the nitrite experiments the quantity of nitric oxide evolved at 19·3° under liquid paraffin B.P. is nearly proportional to the sum of the yields at 0° of

FIG. 3.
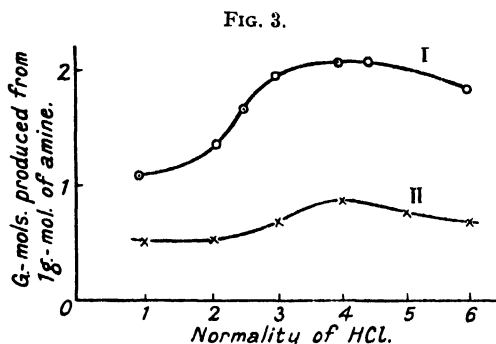
I. *Nitric oxide.*
II. *Sum of nitroamine and dinitro-compound.*

nuclear nitro-compound and nitrosoamine, the fission product being formed without evolution of gas. The equations

$$R\cdot NMe_2 + 4HNO_2 \longrightarrow R\cdot N(NO)Me + MeNO_3 + 2NO + 2H_2O$$
$$R\cdot NMe_2 + 3HNO_2 \longrightarrow NO_2\cdot R'\cdot NMe_2 + 2NO + 2H_2O$$

represent the stoicheiometric proportions, but are of too high an order to be probable as a guide to the mechanism, which probably involves consecutive reactions of a lower order. Since 70% of the gas was evolved in about 7 minutes (mechanical stirring), the reactions involved must be rapid. The blank experiment without amine gave a negligible quantity of gas in an hour.

In 6·0, 4·5, 4·0, and 3·0N-hydrochloric acid, the times (t, mins.) taken for evolution of 70% of the total gases were nearly the same, but the speed was diminished in more dilute solutions, as shown below :

G.-mol. NO	1·90 (1·86)	2·09	2·01 (2·07)	1·95	1·65	1·36	1·06
G.-mol. N	0·20 (0·24)	0·11	0·10 (0·11)	0·10	0·10	0·10	0·11
t	5·6	6·6	6·7	6·5	8·9	19·4	37·3
Normality of HCl	6·0	4·5	4·0	3·0	2·4	2·1	0·94

The nitrogen (7 to 17 c.c.) is of uncertain origin, but it would be formed if a small amount of the amine became dealkylated.

These observations can be fairly expressed by the following scheme, in which there is no reaction of a higher order than termolecular; substances favoured by high acidity are on the right (diazonium analogues) and those favoured by lower acidity (diazo-analogues) are on the left. The fission reactions are omitted because all that is known about them is that (1) nitrous acid is the only substance which produces fission and (2) no gas is given off in the process. The formulæ used for the diazo-analogues are conjectural but likely.

The main features are capable of wide extension to cover other classes of amines,

e.g., the velocity measurements for aliphatic amines recorded by T. W. J. Taylor and his collaborators in this Journal in 1925 and the following years.

$$\left[\begin{matrix} R \cdot NMe_2 \\ \mid \\ H \end{matrix} \right] Cl$$

$\downarrow$ + HNO,

$$\begin{matrix} R \cdot N \cdot Me \\ \mid \\ MeO \cdot N \cdot Cl \end{matrix} \quad \longleftarrow \quad \longrightarrow \quad \left[\begin{matrix} R \cdot NMe_2 \\ \mid \\ NO \end{matrix} \right] Cl$$

+ HNO, at lower temperatures

+ HNO, at 0° without gas

$\downarrow$ + HNO,

$$\begin{matrix} R \cdot N \cdot Me \\ \mid \\ MeO \cdot NO \cdot NO \end{matrix}$$

+ 2HNO,

with evolution of $\longrightarrow$
2NO + H$_2$O

$$\left[\begin{matrix} R \cdot NMe_2 \\ \mid \\ NO_2 \end{matrix} \right] Cl$$

$\downarrow$ + 2HNO,

$$\begin{matrix} R \cdot N \cdot Me \\ \mid \\ MeO \cdot NO \cdot NO_2 \end{matrix} (+ 2NO + H_2O)$$

$\downarrow$ high acidity

$$\left[\begin{matrix} (NO_2)R' \cdot NMe_2 \\ \mid \\ H \end{matrix} \right] Cl$$

$\downarrow$

$$\begin{matrix} R \cdot N \cdot Me \\ \mid \\ NO \end{matrix} (+ Me \cdot O \cdot NO_2)$$

Lower acidity   Higher acidity
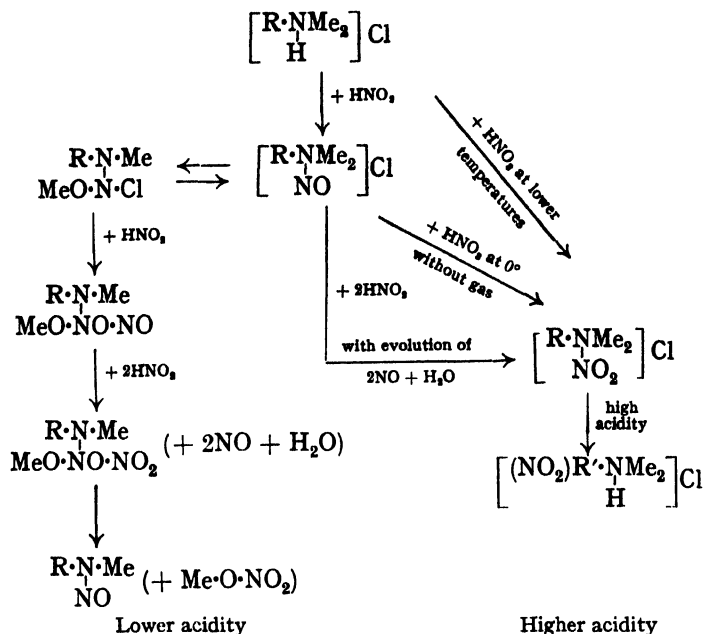
EXPERIMENTAL.

4 : 4'-Bisdimethylaminodiphenylmethane was prepared according to Mohlau and Heinze (*Ber.*, 1902, **35**, 359) and before use was recrystallised from ethyl and from methyl alcohol; m. p. 91° (Found : C, 79·9; H, 8·6. Calc. : C, 80·2; H, 8·6%).

Preparation of Solutions.—40·000 G. of the above base were dissolved and made up to 1 l. in 11·63N-hydrochloric acid. 25·0 C.c. portions of this solution were diluted with water to give a range of hydrogen chloride concentrations from 9·035N to 0·663N, allowance being made for the acid used up by the sodium nitrite (4 mols.), for that used by the base in forming its dihydrochloride (2 mols.), and for the water in which the nitrite was dissolved. Each solution was cooled in ice-water, 5 c.c. of a sodium nitrite solution added containing 4·01 mols. of nitrite to 1·0 mol. of the base, and the reaction continued for 24 hours. The reaction mixture consisted of a precipitate and a solution, each of which was analysed.

Analysis of the precipitate. The precipitate, consisting of the bisnitrosoamine and *p*-nitrodimethylaniline, was collected on a Jena glass filter crucible, washed with 200 c.c. of ice-cold water, dried at 40°, and weighed. The *p*-nitro-compound was then dissolved in 5·5N-hydrochloric acid and the bisnitrosoamine (washed and dried as before) was weighed, a correction being applied for its solubility in 5·5N-hydrochloric acid : it crystallised from methyl or ethyl alcohol in straw-yellow needles, m. p. 102° (compare Pinnow, *Ber.*, 1894, **27**, 3867) (Found : C, 63·1; H, 5·6. Calc. : C, 63·3; H, 5·6%). The *p*-nitrodimethylaniline was estimated by difference, its solubility in the reaction mixture being allowed for : after crystallisation from ethyl alcohol it had m. p. and mixed m. p. 163°.

Solubility of p-*nitrodimethylaniline and of* 4 : 4'-*bismethylnitrosoaminodiphenylmethane in* 100 *c.c. of hydrochloric acid of various concentrations at* 0°.

(1) *p*-Nitrodimethylaniline.

Normality of HCl	3·620	2·439	1·796	1·198	0·898	0·787
Solubility in grams	0·460	0·086	0·043	0·019	0·011	0·008

(2) 4 : 4'-Bismethylnitrosoaminodiphenylmethane.

Normality of HCl	5·939	5·344	4·443	3·819	2·853	1·326
Solubility in grams	0·036	0·031	0·014	0·010	0·008	0·006

Analysis of the filtrate after removal of the insoluble reaction products. The nitration product of the reaction, 3 : 3'-dinitro-4 : 4'-bisdimethylaminodiphenylmethane (Pinnow, *Ber.*, 1894, **27**, 3165), was precipitated by sodium hydroxide as a viscous oil, which crystallised from alcohol or glacial acetic acid in slender red needles, m. p. 124° (Found : C, 59·1; H, 5·8. Calc. : C, 59·3; H, 5·8%).

Since accurate weighing of the oily product was impracticable, the acid filtrate was treated with urea at 25—30° to destroy any nitrous acid and made up to standard bulk by addition of dilute hydrochloric acid, and the nitrate estimated in a portion by titanous chloride. The organic dinitro-compound was similarly determined by titanous chloride at 100° (see Knecht and Hibbert, " New Reduction Methods in Volumetric Analysis ").

Laboratory Preparation of p-Nitrodimethylaniline.—100 G. of 4 : 4'-bisdimethylamino-diphenylmethane are dissolved in 300 c.c. of concentrated hydrochloric acid and cooled to 0°, 800 c.c. of water added, and 100 g. of sodium nitrite in 200 c.c. of water slowly poured into the solution. After 1 hour's stirring, 28 g. of *p*-nitrodimethylaniline are obtained, m. p. 159°. After one crystallisation from glacial acetic acid the product may be taken as pure.

Action of Nitrous Acid on 4 : 4'-Bisdimethylaminobenzophenone.—The ketone, kindly supplied for research purposes by Imperial Chemical Industries Ltd., melted at 179° after repeated crystallisation from ethyl alcohol (Found : C, 76·0; H, 7·3; N, 10·4. Calc. : C, 76·1; H, 7·5; N, 10·4%)

Preparation of Solutions.—12·50 G. of the ketone were dissolved and made up to 500 c.c. with 11·55N-hydrochloric acid. 20 C.c. portions of this solution were diluted with water to give a range of acid concentration from 9·18N to 0·46N, allowances being made for acid used by nitrite, etc., as in the experiments with 4 : 4'-bisdimethylaminodiphenylmethane. Each solution was treated in an exactly similar manner to that previously described under the " methane base " experiments.

All the products of the reaction, being weakly basic, were precipitated from solution. The feebly basic bisnitrosoamine separated even in the strongly acid solutions and the more basic mononitrosoamine was precipitated on dilution with water.

Analysis of the precipitate. The precipitate, consisting of a mixture of mono- and bis-nitrosoamines, was collected on a tared Jena glass filter, washed with 200 c.c. of ice-cold water, and dried at 60°. The mononitrosoamine was removed by allowing 50 c.c. of 5N-hydrochloric acid to percolate through the crucible, and the bisnitrosoamine (washed and dried as before) was weighed, a correction being applied for its solubility in 5N-hydrochloric acid. The mono-nitroso-compound was estimated by difference, its solubility in the reaction mixture being allowed for : it crystallised from ethyl alcohol in bright yellow plates, m. p. 183° (compare Herzberg and Polonowsky, *Ber.*, 1891, **24**, 3198) (Found : C, 70·3; H, 6·2; N, 15·4. Calc. : C, 70·3; H, 6·4; N, 15·3%).

4 : 4'-Bismethylnitrosoaminobenzophenone crystallised from benzene in pale yellow needles, m. p. 234° (compare v. Braun, *Ber.*, 1904, **37**, 2677) (Found : C, 60·4; H, 4·7; N, 18·8. Calc. : C, 60·3; H, 4·7; N, 18·9%).

Solubility of 4 : 4'-bismethylnitrosoaminobenzophenone and of 4-dimethylamino-4'-methylnitroso-aminobenzophenone in 100 c.c. of hydrochloric acid of various concentrations at 0°.

(1) The bismethylnitrosoamine.

Normality of HCl	7·58	5·05	3·79	2·53	0·76
Solubility in grams	0·034	0·025	0·020	0·019	0·018

(2) The monomethylnitrosoamine.

Normality of HCl	5·68	3·79	2·53	1·52	0·76
Solubility in grams	large	0·671	0·127	0·045	0·037

Action of Nitrous Acid on 4 : 4'-Bisdiethylaminodiphenylmethane.—To 5 g. of the base, dissolved in 100 c.c. of 11·5N-hydrochloric acid and diluted with 30 c.c. of water, a solution of 4·5 g. of sodium nitrite in 10 c.c. of water was slowly added at 0°. Evolution of nitric oxide proceeded steadily for hours; the solution turned red, and after 90 minutes began to precipitate 4 : 4'-bisethylnitrosoaminodiphenylmethane, of which 0·5 g. had separated as colourless plates after 24 hours; it melted at 83° after crystallisation from alcohol and gave the Liebermann nitroso-reaction strongly (Found : C, 65·3; H, 6·4; N, 17·8. $C_{17}H_{20}O_2N_4$ requires C, 65·4; H, 6·4; N, 17·9%).

Neutralisation of the remaining solution precipitated 4·5 g. of an oil, which solidified in

red needles soluble in ether and sparingly soluble in alcohol or glacial acetic acid, melted at 39—40° after crystallisation from alcohol, did not give the Liebermann nitroso-reaction, and consisted of *dinitro-*4 : 4′-*bisdiethylaminodiphenylmethane* (the nitro-groups are probably in positions 3 and 3′) (Found : C, 62·8; H, 7·2; N, 14·1; NO_2, 22·7. $C_{21}H_{28}O_4N_4$ requires C, 63·0; H, 7·0; N, 14·0; NO_2, 23·0%).

In a similar experiment with 50 c.c. of hydrochloric acid and 150 c.c. of water, the gassing was less vigorous and precipitation began in 20 minutes. After 24 hours, 1·3 g. of a mixture, m. p. 70—80°, had been precipitated. This was dissolved in hydrochloric acid; cautious addition of water then precipitated 0·8 g. of yellow *p*-nitronitrosoethylaniline, m. p. and mixed m. p. 116° (Found : C, 49·3; H, 4·8; N, 21·5. Calc.: C, 49·3; H, 4·6; N, 21·5%). Neutralisation then precipitated 0·5 g. of *p*-nitrodiethylaniline, yellow needles, m. p. 77·5°, and 78·0° after admixture with an authentic specimen (Found : C, 61·8; H, 7·2; N, 12·5. Calc.: C, 61·9; H, 7·2; N, 14·4%). From the original mother-liquor, alkali precipitated 3·5 g. of the same dinitrobisdiethylaminodiphenylmethane as was obtained in the previous experiment.

12. The Kinetics of the Reaction between Hydrogen and Sulphur. Part I. Reaction at 265—350° and 290—820 mm.

By ERNEST E. AYNSLEY, THOMAS G. PEARSON, *and* PERCY L. ROBINSON.

THE investigation of the reaction between hydrogen and sulphur by Bodenstein (*Z. physikal. Chem.*, 1899, **29**, 315) and Norrish and Rideal (*J.*, 1923, **123**, 696) failed to disclose its essential characteristics; we (*Nature*, 1933, **131**, 471) find it to occur in two ways, homogeneously in the gaseous phase, and heterogeneously at the surface of molten sulphur. Each reaction has a uniform temperature coefficient over the range of temperature investigated, and a velocity which is independent of the area and the nature of the glass surface and uninfluenced by hydrogen sulphide or nitrogen. The homogeneous reaction, therefore, is one of the simplest syntheses disclosed by kinetic studies.

The work of Hautefeuille (*Compt. rend.*, 1867, **64**, 610) and of Pélabon (*ibid.*, 1897, **124**, 686) has been discussed by Bodenstein (*loc. cit.*), who, using glass bulbs containing excess of sulphur, obtained equilibrium constants, and deduced the velocity of hydrogen sulphide formation between 234° and 356°. The temperature coefficient per 10° rose from 1·34 at the lower temperature to 1·77 at the higher. Nevertheless, he believed the reaction to be essentially homogeneous and confined to the gaseous phase. His velocities were proportional to the concentration of hydrogen and roughly to the square root of that of the sulphur, for, although he was really dealing with two concurrent reactions, his area of sulphur surface was sufficiently small to render the homogeneous reaction dominant.

Norrish and Rideal's criticism of Bodenstein's method, *viz.*, that hydrogen sulphide liberated by the sulphur on solidification vitiated his equilibrium measurements, seems scarcely warranted in view of the small amounts employed; the criticism, however, that the variable temperature coefficient indicated more than one reaction and that there was no information regarding the possible effect of the glass surface, is pertinent. To avoid difficulty from the solubility of hydrogen sulphide in molten sulphur, Norrish and Rideal employed a dynamic method. They used mixtures of hydrogen and nitrogen, and obtained curved lines on plotting the logarithms of the reaction velocity for the two hydrogen pressures (0·810 atm. and 0·304 atm.) against temperature. The differences of these velocities plotted against temperature gave a straight line, which was interpreted as indicating only a homogeneous reaction between sulphur and hydrogen at 0·506 atm., a reaction at the glass surface, believed to be common to each series, being regarded as independent of pressure. It is doubtful, however, whether Norrish and Rideal worked with hydrogen alone. Moreover, cylinder nitrogen invariably contains oxygen, which would

probably not be completely removed by their method of purification, and the curvature must, in our judgment, be ascribed to such traces of oxygen and not to the incidence of a surface reaction. Indeed, we have shown this effect to be eliminated by rigorous removal of oxygen. Their results for the concentrations under consideration differ from ours also in respect of (1) an alleged heterogeneous reaction on the glass, of which we have found no trace, and (2) the heterogeneous reaction at the surface of molten sulphur, which they failed to observe.

During the progress of the present investigation, Kassel ("Kinetics of Homogeneous Gas Reactions," pp. 159—162) has criticised Norrish and Rideal's treatment of their data, and has drawn attention to the absence of experiments with pure hydrogen. These matters are discussed at greater length below, and general difficulties attending dynamic methods are pointed out.

EXPERIMENTAL.

Purification of Materials.—Hydrogen was prepared from arsenic-free zinc and hydrochloric acid, and gave a negative Marsh test. As our experiments indicated the necessity for the complete removal of oxygen, the following methods were used : (i) passage through heated platinised asbestos, and then through almost colourless, alkaline pyrogallol; (ii) treatment with chromous chloride and amalgamated zinc (Carter and Hartshorne, J., 1926, 363; Hartshorne and Spencer, *J. Soc. Chem. Ind.*, 1926, **45**, 474). Reaction velocities with hydrogen purified by each method were the same, except at the lowest temperature, 280°, where that from pyrogallol gave a value higher, in a 49 c.c. bulb, by 0·5 c.c. of 0·001N-iodine, which is sufficient to disturb the strict linearity of the $d \log [H_2S]/dT$ function. With hydrogen treated with chromous chloride, this linearity was maintained.

These methods, except passage through platinised asbestos, were also employed for the nitrogen mixtures. The gases were washed with aqueous potash to remove acid spray coming from the chromous chloride, and passed through potash pellets and phosphoric oxide immediately before use.

Nitrogen. Cylinder nitrogen, containing 6% of oxygen, was treated with alkaline pyrogallol either alone or followed by chromous chloride.

Sulphur. Roll sulphur was refluxed in a Pyrex flask under dry carbon dioxide for several days, black material separating. It was distilled thrice in carbon dioxide and twice in pure nitrogen, with rejection of appreciable head and tail portions, and finally fractionated five times in a vacuum.

TABLE I.

Fall in Velocity of Hydrogen Sulphide Formation with Time.

Temp. = 290°.

Duration of heating, hrs.	1	2	3	4	5	6
Velocity of H_2S formation, g./sec. $\times 10^8$	2·36	2·03	1·89	1·84	1·75	1·61

Dynamic Method.—The method first used was identical with that of Norrish and Rideal, but this procedure was considerably modified for the following reasons. (i) The velocity of hydrogen sulphide formation diminishes with time, owing to the transfer of sulphur from the body to the neck of the flask; this is illustrated by Table I and is more marked the higher the temperature. (ii) The colorimetric estimation of hydrogen sulphide is untrustworthy through (a) the rapid atmospheric oxidation of the alkaline sulphide, (b) the difficulty of matching intensities, the colour of the suspension being brown when produced by excess lead and greyish-black by excess sulphide. (iii) It is difficult to maintain a constant streaming rate of hydrogen by a screw clip on rubber tubing.

Apparatus and manipulation. Our new Pyrex reaction vessel (Fig. 1) allowed hydrogen to enter at *C*, pass down the annulus *P* into the bulb *A*, and emerge *via* the annulus *Q* to *D*. The inner tube, *F*, expanded at *G*, served as a reservoir for replenishing the parallel-sided well, *B*. After being cleaned and dried, the vessel was charged with sulphur, evacuated, filled with hydrogen and emptied several times to remove oxygen, and again evacuated. The sulphur was boiled twice in a vacuum, dissolved gases being removed. After being cooled, the vessel was refilled with hydrogen and incorporated in the system, the tube, beyond tap T_2, being connected to a source of hydrogen. The system was swept out over-night with hydrogen and afterwards evacuated through both T_1 and *D*. The sulphur was just melted and, by adjustment

of hydrogen pressures, assumed the position indicated in Fig. 1; after cooling, it remained solid in *G* even with the vessel in the heating bath. The well was replenished by melting the sulphur and allowing sufficient to flow into it. The reaction vessel was submerged in the bath of fused sodium and potassium nitrates to the depth indicated, the exposed portion being cooled by an air current directed into an aluminium cup. Temperatures within $\pm 0.25°$ of those required were maintained by manual control.

Tests showed that iodine is removed from $0.02N$- and weaker iodine solutions containing 10 g. of potassium iodide per litre by a hydrogen stream, but not from such solutions when starch is present. The estimation of iodine by the thiosulphate titration, against a white background,
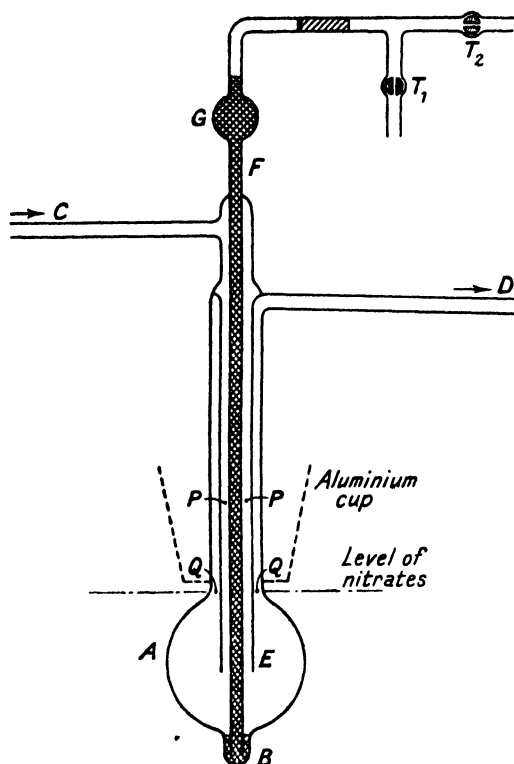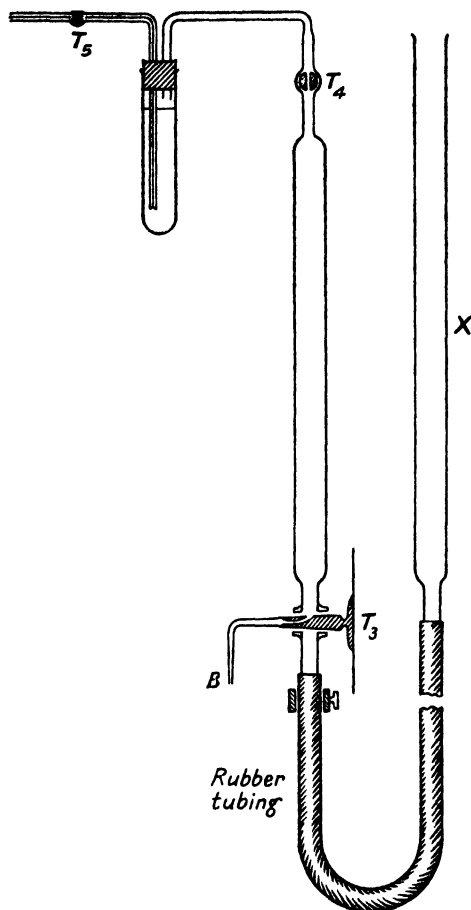

FIG. 1.   FIG. 2.

gave end-points accurate to ± 0.1 c.c. of $0.001N$. Standard solutions less concentrated than $0.1N$ were prepared and checked immediately before use. The ultimate standard employed was pure potassium dichromate.

Regular and accurately known streaming velocities were given by a Hempel burette (Fig. 2) fitted with a fine jet at *B*. The velocity of aspiration was governed by regulating T_3 so that the gas in the burette increased uniformly with time, and, finally, the volume of the gas employed in the run was measured at atmospheric pressure. Since alteration from 50 to 100 c.c. per hour in the streaming rates did not change the velocity of the reaction, the convenient rate of 75 c.c. per hour was adopted.

The reaction vessel was swept out for 12 hours at approximately the velocity and slightly below the temperature to be employed in the run, and finally for 2 hours under precisely these conditions, with hydrogen which had passed (i) through 1 m. of alkaline pyrogallol, (ii) over 10 cm. of heated platinised asbestos, (iii) through 25 cm. of potash pellets, followed by 50 cm.

of phosphoric oxide. The velocities recorded are means of six or more individual determinations of which the set of six (Table II) is representative.

TABLE II.

Temp. 599·9° Abs.   Duration of run, 60 mins.

Vol. of H_2 collected in burette, c.c..............	75·1	75·0	75·2	75·3	75·1	75·2	
0·01N-Iodine used, c.c.	11·9	11·8	11·8	11·8	11·9	11·8	
Velocity of H_2S formation, g./sec. × 10^8 ...	56·2	55·7	55·7	55·7	56·2	55·7	Mean 55·9

It was known (see below) that the reaction velocities varied with the area of liquid sulphur, and the values below were those obtained with 1·02 sq. cm. area of liquid in (a) hydrogen at atmospheric pressure and (b) a mixture of hydrogen and nitrogen (not treated with chromous chloride). When the logarithms of the velocity are plotted against $1/T$, the data of Table III (a) give an almost straight line, whilst those in Table III (b) give a curve.

TABLE III.

Velocities of H_2S *Formation.*

(*Surfaces of liquid sulphur and of glass constant.*)

(a) *In pure hydrogen.*

Temp., Abs.	538·7°	553·7°	569·0°	584·3°	599·9°	621·3°
Total press. of H_2 plus S vapour at temp. of expt., mm..	779	774	767	784	784	777
Mean velocity of H_2S formation, g./sec. × 10^8	1·42	3·63	8·50	22·9	55·9	189·0

(b) *In hydrogen–nitrogen mixture* (40 : 60 by vol.).

Temp., Abs.	538·7°	553·7°	569·0°	584·3°	599·9°	621·3°
Total press. of H_2 plus S vapour at temp. of expt., mm..	752	756	762	758	766	754
Mean velocity of H_2S formation, g./sec. × 10^8	0·76	1·51	3·76	8·40	18·9	64·7

The glass surface was increased by 500% by packing with round-ended lengths of Pyrex rod, not touching the liquid. (Runs with shorter rods partly covering the liquid surface showed a diminished velocity.) The gaseous volumes of both the packed and the empty reaction chamber were identical, and the following velocities show that the additional surface is without effect :

Temp. 569° Abs.   Area of liquid sulphur pool constant.

Condition of vessel.	Mean rate of H_2S formation, g./sec. × 10^8.
Without glass rods...	15·8
Packed with glass rods clear of sulphur pool...........................	15·7
„ „ „ partly covering sulphur pool	12·2

To investigate the behaviour of liquid sulphur, a Pyrex Claisen flask was charged with 1 g. of sulphur, from which gas was removed by boiling in a vacuum. The sulphur solidified on the bottom in a circular pool, the area of which could be ascertained with reasonable accuracy. After a maturing period of 12 hours at just below 296°, runs were made at this temperature. Successively larger amounts of sulphur were used but, as anticipated, a quantitative correlation was not obtained. With the larger quantities, however, the velocity was roughly proportional to the area, but as this became less, the ratio of the velocities approached unity, owing to the contribution of the homogeneous reaction (see below).

Relation of Velocity to Area of Liquid Sulphur.

Temp. 569° Abs.   Volume of reaction vessel =·65 c.c.

Area of liquid sulphur pool, sq. cm.	Mean rate of H_2S formation, g./sec. × 10^8.	$\dfrac{\text{Rate}}{\text{Area of pool}}$.
1·13	6·5	5·75
2·69	8·6	3·20
8·76	17·4	1·99

Comparative experiments in identical flasks proved the reaction velocity to be the same in Pyrex, Monax, or soft glasses.

Our dynamic study of the combination of hydrogen and sulphur points to two distinct

reactions : (i) homogeneous, and (ii) heterogeneous at the surface of the liquid. It shows, further, that quantitative investigation of the individual velocities of the two reactions is impossible by this method and indicates, in conflict with Norrish and Rideal's observations, that the velocity is independent of the area of glass surface and varies with the area of the liquid sulphur.

The Static Method.—By carrying out the reaction in bulbs wherein any desired quantity of sulphur may be used, the difficulties caused by the removal of sulphur from the reaction zone, inherent in the dynamic method, are avoided. Especially, the static method allows of working with less than saturated sulphur vapour and, indeed, is only limited by the accuracy obtainable in the evaluation of the reaction products, which, in the present instance, is very high. The reaction was therefore studied in glass bulbs (i) in the gaseous phase alone, (ii) with liquid also present, and (iii) with various volumes and against different areas of glass.

The Homogeneous Reaction.

Glass bulbs, provided with two limbs, were cleaned and closed at one end. After the appropriate weight of sulphur had been added, a capillary was formed on the other limb, and they were attached by rubber to a vacuum train. The train was swept out over-night with hydrogen, and the bulbs were evacuated and filled with hydrogen four times to remove air. The pressures were measured on the manometer, and the bulbs were sealed off under conditions which led to inappreciable changes in pressure on removal. The bulbs were held below the surface of the fused nitrates, and, since the bath is slightly cooled by this operation, the liquid was in such a condition that when equilibrium was reached, the bath and its contents were at the required temperature. The bulbs were cooled in air, washed, and opened beneath standard iodine solution, which entered in a sufficient quantity to react with the hydrogen sulphide; the contents were then washed into a beaker. Control experiments showed that the operation of opening and washing could be accomplished without diminution in the iodine titre. The estimation was concluded by titrating unused iodine with standard thiosulphate.

TABLE IV.

Effect of Sulphur Concentration.

Vol. of standard bulb = 61 c.c.   Hydrogen press. = 357 mm. (at 15°).

Temp. = 574° Abs.   Duration of run = 60 mins.

Wt. of S in bulb, g.	0·0120	0·0085	0·0055
Rate of H_2S formation, g./sec. $\times 10^8$	6·52	5·53	4·44
Rate $\times 10^8/\sqrt{[S]}$	594	599	598

Vol. of standard bulb = 49 c.c.   Hydrogen press. = 382 mm. (at 15°).

Temp. = 595° Abs.   Duration of run = 60 mins.

Wt. of S in bulb, g.	0·0190	0·0150	0·0120	0·0090
Rate of H_2S formation, g./sec. $\times 10^8$	27·2	24·2	21·7	19·0
Rate $\times 10^8/\sqrt{[S]}$	197	197	198	201

Sulphur Concentration.—Table IV shows that, for two temperatures, the velocities are proportional to the square root of the sulphur concentration.

TABLE V.

Effect of Hydrogen Concentration.

Duration of run = 60 mins.

Temp., Abs.	Press. of H_2 in bulb at reaction temp., mm.	Rate of H_2S formation, g./sec. $\times 10^8$.	Ratio of pressures.	Ratio of rates.
573°	760	5·34	2·50	2·48
	304	2·15		
593	787	19·28	2·50	2·51
	315	7·67		

Hydrogen Concentration.—A set of bulbs of uniform volume (49 c.c.) were charged with 0·0120 g. of sulphur, and half were filled with hydrogen at 382 mm. (15·0°) and half at 153 mm. (15·0°). The bulbs were heated, some at 300° and others at 320°, with results (Table V) which prove the velocity of hydrogen sulphide formation to be directly proportional to the pressure of hydrogen.

TABLE VI.

Effect of Hydrogen Sulphide.

Vol. of reaction bulb = 49 c.c.   Wt. of S added = 0·0190 g.

Temp. = 594·6° Abs.

Period of heating bulb, hrs.	1	4	6
Titre, c.c. of 0·001N-I₂	55·3	199·9	283·4
Wt. of H₂S formed, g. × 10⁵	94	340	482
k, calc.	491	485	489

It is evident that a certain amount of sulphur and hydrogen is used up during the course of the reaction so that a slight allowance should be made for this, and, as the effects on the velocity of the reaction of both the sulphur and the hydrogen concentration are known, it is possible to apply this correction. Throughout the investigation, however, the decrease in the concentration of reactants was usually only 1—2% in any run, and therefore the means of the initial and final concentrations of hydrogen and sulphur were employed as the effective concentrations to which the velocities were related.

Effect of Hydrogen Sulphide.—Since the velocity of hydrogen sulphide formation is proportional both to the concentration of hydrogen and to the square root of that of the sulphur, then, provided the velocity be uninfluenced by the accumulated hydrogen sulphide, if x is the amount of hydrogen sulphide formed after time t,

$$dx/dt = k(\sqrt{[S]} - x)([H_2] - x)$$

This on integration gives

$$k = \frac{2}{t\sqrt{[H] - [S]}} \tan^{-1} \frac{(\sqrt{[H] - [S]})(\sqrt{[S]} - \sqrt{[S]} - x)}{([H] - [S]) + (\sqrt{[S]} . \sqrt{[S] - x})},$$

an expression amenable to experimental verification.

Three bulbs with 0·0190 g. of sulphur and hydrogen at 382 mm. (at 15·0°) were heated at 321·6° for 1, 4, and 6 hours respectively, and the hydrogen sulphide formed was determined. These quantities (Table VI) show that hydrogen sulphide up to 15·7% by volume is without effect on the velocity of the reaction at this temperature and pressure.

Effect of Glass Surface.—By introducing glass rods into a 63 c.c. bulb, its capacity was reduced to the standard 49 c.c., and the glass surface was increased five-fold. Rods with rounded ends were used in order to preserve the fire-polished surface. In one series, 0·0120 g. of sulphur, insufficient to leave any liquid at 301°, was employed, and in another 0·0300 g., enough to provide a slight residue of liquid at 322°. The results show that the rate is independent of the surface :

Wt. of H₂S formed, g./sec. × 10⁸.

Temp., Abs.	(a) Without rods.	(b) With rods.	Diff., %.
574°	5·62	5·57	— 0·89
595	28·60	28·70	+ 0·35

Influence of Volume.—Runs in bulbs of volume ranging from 47 to 225 c.c. with uniform concentrations of both sulphur and hydrogen were made at several temperatures and the velocities were proportional to the volume. Corrections may thus be applied for bulb volume.

Temp., Abs.	Press. of H₂ at 15·0°, mm.	Vol. of reaction bulb, c.c.	Wt. of S, g.	Wt. of H₂S formed, g./sec. × 10⁸.	Wt. (g. × 10¹¹) of H₂S formed per sec. per c.c. of gaseous vol.
595°	382	49	0·0120	21·7	442
		225	0·0551	99·3	441
616	382	49	0·0120	73·6	150
		225	0·0551	336·7	150
563	153	49	0·0120	1·1	22·4
		225	0·0551	5·0	22·2
595	153	49	0·0120	8·4	171
		225	0·0551	38·2	170

Temperature Coefficient of the Homogeneous Reaction.—Velocities were measured at temperatures between 280° to 343° at two concentrations of hydrogen, and, except at 280°, with one concentration of sulphur (0·0120 g. in a 49 c.c. bulb); since this amount of sulphur would have given some liquid at this temperature, less solid was used, and the velocity obtained was

scaled to correspond to that from the normal concentration (0·0120 g./49 c.c.) by multiplying it by the square root of the ratio of the two concentrations, thus making this result comparable with the others.

Temp., Abs.		553°	558°	563°	574°	584·5°	595°	616°
Wt. of H_2S formed, g./sec. $\times 10^{10}$/c.c. of gaseous volume, at a hydrogen pressure (measured at 15°) of	382 mm.	2·77	3·89	5·49	11·47	22·66	44·23	150·2
	153 mm.	1·13	—	2·22	4·63	9·06	17·16	59·36

Plots of the logarithms of the velocities against the reciprocal of the absolute temperature (Fig. 3) proved to be parallel straight lines, and point to a single reaction of which the temperature coefficient is 1·90 per 10°, and the heat of activation 43·3 kg.-cals.

Influence of Minute Traces of Oxygen in the Nitrogen–Hydrogen Mixtures.—Hydrogen and nitrogen (40 : 60, by vol.) which had each passed through 1 m. of alkaline pyrogallol were mixed and, immediately before entering the reaction bulbs, were bubbled slowly through two 1 m. lengths of alkaline pyrogallol followed by the usual drying tubes. Results, Table VII, gave, when the logarithms of the velocities were plotted against $1/T$, a curve (*A*, Fig. 4) which, by
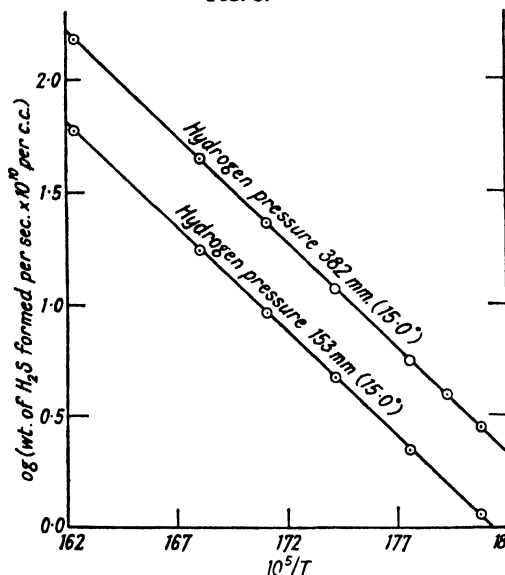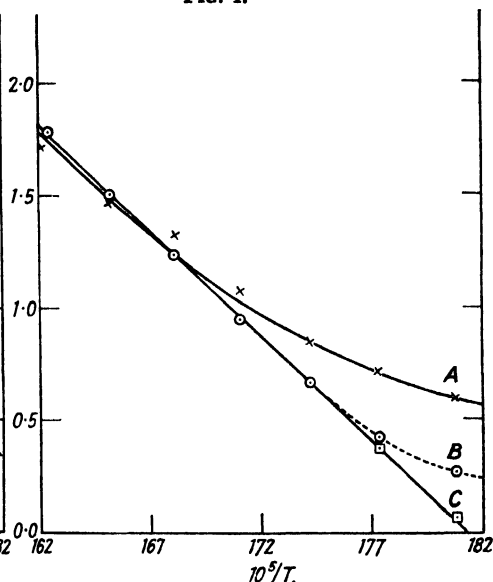
FIG. 3.

FIG. 4.

comparison with the straight line from pure hydrogen (*i.e.*, line 153 mm. in Fig. 3), indicated an increase in the velocity which was very pronounced at the lower temperatures but vanished at the highest temperatures. (The slightly low values at the higher temperatures are due to interaction between the hydrogen sulphide and the sulphur dioxide, whereby the apparent yields are lessened—see Part II.) This led to further treatment for the removal of oxygen. In the first case the above mixture was allowed to stand in the gas-holder over alkaline

TABLE VII.

Influence of Minute Trace of Oxygen.

Press. of H_2-N_2 mixture = 382 mm. (at 15·0°).   S concn. = 0·0120 g./49 c.c.

Temp., Abs.	Wt. of H_2S formed, g./sec. $\times 10^{10}$/c.c. of gaseous volume, H_2-N_2 mixture having been treated		
	(*a*) ordinarily.	(*b*) with alk. pyrogallol.	(*c*) with chromous chloride.
553°	3·92	1·86	1·66
564	5·14	2·63	2·40
575	6·96	4·63	—
584·5	11·7	8·88	—
595	20·6	17·2	—
605·3	29·5	31·7	—
616	—	61·1	—
617	51·8	—	—

pyrogallol and, immediately before use, was passed through two 1 m. lengths of pyrogallol and a special form of gas-washer (Parker and Robinson, J., 1929, 1106). The results (*B*, Fig. 4) were now identical with those from pure hydrogen except at 290° and 280°, where a slight increase was still apparent. In consequence, each gas was individually passed through 1 m. of chromous chloride before mixing and, immediately prior to use, the mixture was passed through two 1 m. tubes containing the chromous chloride–amalgamated zinc reagent; the results (*C*, Fig. 4) were then almost identical with those from pure hydrogen at the lowest temperatures. Evidently the reaction is unaffected by nitrogen, which acts simply as a diluent.

The Heterogeneous Reaction on the Liquid Sulphur.

The contribution of the homogeneous reaction to the composite velocity now being known, the investigation of the reaction at the surface of liquid sulphur became possible. For this, vessels of identical volume, provided with wells so shaped that equal quantities of liquid presented different areas, were used. The volume of the liquid, as distinct from its exposed surface, was shown to be without effect on the reaction.

Hydrogen press. = 382 mm. (at 15·0°). Temp. = 584·5° Abs.

Wt. of S, g.	Surface area of pool, sq. cm.	Gaseous vol. above pool, c.c.	Wt. of H_2S formed from composite reactions, g./sec. $\times 10^8$.
4·5	4·75	122·7	40·1
3·0	4·75	122·7	40·3

The homogeneous reaction was first measured in saturated sulphur vapour at appropriate temperatures and pressures. Subsequently, 4·5-g. lots of sulphur were weighed into bulbs. These were attached to the charging train, evacuated after several washings with hydrogen, and finally the sulphur was boiled in a vacuum to facilitate drying and degassing. Sulphur which had condensed on the sides of the bulb was subsequently returned to the well by warming with a Bunsen flame, so that the pool had a well-defined area. The vessels after cooling were filled with hydrogen, sealed, and heated, with precautions against alteration of the areas of sulphur surface when melting occurred.

The contribution of each reaction to the total velocity was computed by two methods : (i) the experimentally determined gaseous velocity, corrected to the particular volume under consideration, was deducted from the composite velocity; (ii) the simultaneous equations based on the composite velocities with either different areas of sulphur or different working volumes were solved.

FIG. 5.

Temp. = 584·5° Abs. Hydrogen press. = 382 mm. (at 15·0°).

Surface area of S pool, sq. cm.	Gaseous vol. above pool, c.c.	Yield of H_2S from composite reaction, g./sec. $\times 10^8$.
4·75	122·7	0·401
9·84	129·7	0·476

If x and y are the number of g. of H_2S formed per sec. respectively in each c.c. of saturated sulphur vapour and on each sq. cm. of liquid sulphur surface; then

$$122\cdot7x + 4\cdot75y = 0\cdot401 \times 10^{-6}$$
$$129\cdot7x + 9\cdot84y = 0\cdot476 \times 10^{-6}$$

whence $\quad x = 0\cdot286 \times 10^{-8}$ (Found : $0\cdot285 \times 10^{-8}$ g.)

and $\quad y = 0\cdot108 \times 10^{-7}$

so the yield per sec. of the H_2S from a surface of 4·75 sq. cm. = $4\cdot75y = 0\cdot511 \times 10^{-7}$ g. (Found : $0\cdot519 \times 10^{-7}$ g.), and yield per sec. of H_2S from a surface of 9·84 sq. cm. = $9\cdot84y = 1\cdot06 \times 10^{-7}$ g. (Found : $1\cdot07 \times 10^{-7}$ g.).

The concordance (Table VIII) is good, and sufficient to permit an estimate of the velocity of the heterogeneous reaction at the surface of liquid sulphur. The results, plotted in Fig. 5,

F

<div align="center">TABLE VIII.</div>

<div align="center">*Heterogeneous Reaction.*</div>

Temp., Abs.	H_2 press., mm. at 15·0°.	Area of liquid pool, sq. cm.	Gaseous vol. above pool, c.c.	Rate of composite reaction, g. H_2S/ sec. × 10¹⁰.	Velocity of gas reaction for saturated S vapour, g./sec. × 10¹⁰/c.c. of gaseous volume.		Surface yields, g. H_2S/sec. × 10¹⁰.	
					Found.	Calc.	Found.	Calc.
595°	382	4·75	122·7	8220	58·4	58·8	1050	1010
		9·29	132·7	9760			2010	1970
584·5	382	4·75	122·7	4010	28·5	28·6	519	511
		9·84	129·7	4760			1070	1060
574	382	4·75	122·7	1880	13·1	13·2	262	251
		10·20	132·7	2300			551	539
595	153	4·75	122·7	3290	23·3	23·4	425	415
		9·29	132·7	3920			826	811
584·5	153	4·75	122·7	1600	11·3	11·4	217	198
		9·84	129·7	1890			430 ,	410
574	153	4·75	122·7	767	5·4	5·4	104	105
		9·84	129·7	917			215	217

show that the reaction is proportional to the area of liquid sulphur and also to the hydrogen pressure. The temperature coefficient is 1·95 per 10°, and the heat of activation 45·5 kg.-cals.

Influence of Nitrogen.—Pure nitrogen does not affect the composite velocity (Table IX), and since it does not affect the homogeneous reaction, it follows that the surface reaction is also unaffected.

<div align="center">TABLE IX.</div>

<div align="center">*Influence of Nitrogen.*</div>

<div align="center">Press. of H_2–N_2 mixture (40 : 60 by vol.) = 382 mm. at 15·0°.</div>

Temp., Abs.	Area of liquid pool, sq. cm.	Gaseous vol. above pool, c.c.	Composite reaction (g. H_2S/sec. × 10⁹) with	
			H_2–N_2 mixture.	pure H_2 at corresponding press.
574°	4·75	122·7	78	77
584·5	4·75	122·7	159	160
595	4·75	122·7	324	329

Pyrex glass was adopted as standard in this work, but the results given below show that Monax and soft glasses may be used without affecting either the homogeneous or the heterogeneous reaction.

<div align="center">Press. of H_2 = 382 mm. at 15·0°. Area of S. pool = 1·08 sq. cm. Gaseous vol. above pool = 49 c.c.</div>

Glass...	Soft.	Monax.	Pyrex.
Composite reaction, g. H_2S/sec. × 10⁹	151	151	157

<div align="center">DISCUSSION.</div>

We have found the reaction between hydrogen and sulphur under the present conditions to proceed only in the gas phase, or at the sulphur surface. Neither reaction is influenced by glass or the presence of nitrogen or hydrogen sulphide. The effect of oxygen and sulphur dioxide will be dealt with in Part II.

The velocity of the homogeneous reaction (temperature coefficient 1·90; heat of activation 43·3 kg.-cals.) is proportional to the square root of the sulphur concentration and to the hydrogen concentration; hence

$$dx_1/dt = k_1[S]^{\frac{1}{2}}[H_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The velocity of the heterogeneous reaction (temperature coefficient 1·95; heat of activation 45·5 kg.-cals.) is proportional to the area of the surface of molten sulphur (A) and to the hydrogen concentration, and is independent of the vapour pressure of the sulphur; hence

$$dx_2/dt = k_2A[H_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Our knowledge of the equilibria in sulphur vapour is imperfect, and attempts to evaluate the equilibrium constants, and therefrom the partial pressure of the individual molecular

species, involve some uncertainty (compare Preuner and Schupp, *Z. physikal. Chem.*, 1909, **68**, 129). Although, for this reason, a full interpretation of the data is necessarily tentative, points emerge for which considerable probability may be claimed. There is little foundation, for example, for Bodenstein's suggestion that the occurrence of the $\sqrt{S}$ function in the velocity equation implies the mechanism $H_2 + S \longrightarrow H_2S$, which, from other considerations, was also adopted by Norrish and Rideal. It rests on Bodenstein's assumption that the last step of the chain $S_8 \rightleftharpoons 2S_4 \rightleftharpoons 4S_2 \rightleftharpoons 8S$ is the one which immediately precedes combination. Actually, $S_4 \rightleftharpoons S_2$ may be responsible, and is the more likely for two reasons : (*a*) at the pressures used, the concentration of sulphur atoms is negligibly small, and (*b*) the reaction $H_2 + S \longrightarrow H_2S$ can only result from three-body collisions, which are too rare to account for the yields. The reaction $H_2 + S_2 \longrightarrow$ $H_2S + S$, however, occurs without the intervention of a third body, little difficulty being presented by the removal of the liberated sulphur atom by collisions which will occur with other particles. Moreover, the absence of chains of appreciable length discounts the possibility of such mechanisms as

$$H_2 + S \longrightarrow SH + H, \qquad HS + H_2 \longrightarrow H_2S + H$$
$$H + S_x \longrightarrow HS + S_{x-1} \qquad H + S_2 \longrightarrow HS + S$$

which alone, on the sulphur atom hypothesis, would account for the hydrogen sulphide formed. The evidence favours the sequence

$$1. \quad H_2 + S_2 \longrightarrow H_2S + S$$
$$2. \begin{cases} S + S_x \longrightarrow yS_{(x+1)/y} \\ S + H_2 + M \longrightarrow H_2S + M' \end{cases}$$

rather than a process initiated by sulphur atoms. It should be emphasised, however, that anything more than a tentative suggestion of the probable mechanism must await precise knowledge of the molecular constitution of sulphur vapour and its dependence on temperature and pressure.

It is impossible to state a mechanism for the heterogeneous reaction in the absence of any knowledge of the nature of the sulphur surface. A striking feature of the reaction is that the temperature coefficient is almost identical with that of the gas reaction, which probably indicates that the reaction is of the same type, and lends support to our contention that it is not between sulphur atoms but rather between S_2 molecules and hydrogen, since it is improbable that sulphur atoms are present in liquid sulphur. The fact that the reaction is independent of the concentration of sulphur vapour in the body of the vessel shows that it arises from sulphur " in the surface " or immediately released therefrom.

The mechanism previously proposed by Norrish and Rideal is based on data which we have been unable to confirm. There are, moreover, some points in their treatment of the results which are open to criticism.

(1) Their assessment of the vapour pressure of sulphur assumes that $[S_8]/[S]$ is independent of temperature, *i.e.*, that the heat of dissociation of gaseous S_8 is zero, which involves an error of 60 kg.-cals. and also involves the employment of $[S]^{\frac{1}{2}}$ instead of $[S]^{\frac{1}{4}}$.

(2) No allowance is made for the fall in concentration of hydrogen with rising temperature consequent upon the increase in sulphur concentration.

(3) They found the heat of activation of the gas reaction to be 52 kg.-cals., whereas " from the data of Preuner and Schupp it is possible to calculate a rather uncertain value for the heat of vaporisation of S_2 at 350° C., namely, 28 kg.-cals. The heat of dissociation of S_2 is somewhat better known, being 102·5 kg.-cals. Thus the heat of vaporisation of S atoms from liquid sulphur at 350° must be about 65 kg.-cals. Since it is very unlikely that the true reaction has a negative temperature coefficient, the suggestion that S atoms are involved must be dismissed " (Kassel, *op. cit.*).

The flow method suffers from serious difficulty when employed with a volatile material, such as sulphur, in that (i) useful investigation in the gaseous phase is limited to the saturated vapour only and (ii) the area of reacting surface, whether solid or liquid, is difficult to assess precisely.

Mr. E. A. O'Connor, of Queensland University, Brisbane, who has very kindly communicated to us the results of an independent investigation of the reaction by a dynamic method, has also failed to find evidence of a reaction at the glass surface.

SUMMARY.

1. The reaction between hydrogen and sulphur has been investigated by a dynamic and by a static method. The former is incapable of dealing fully with the problem, but the latter proved adequate.

2. Hydrogen and sulphur react (i) homogeneously, with a velocity proportional to the concentration of hydrogen and to the square root of that of sulphur (temperature coefficient 1·90; heat of activation 43·3 kg.-cals.); (ii) heterogeneously, with a velocity proportional to the concentration of hydrogen and to the area of liquid sulphur (temperature coefficient 1·95; heat of activation 45·5 kg.-cals.).

3. The following mechanism has been tentatively suggested for the gas reaction :

$$\text{(i)} \quad H_2 + S_2 \longrightarrow H_2S + S$$

$$\text{(ii)} \begin{cases} S + S_x \longrightarrow yS_{(x+1)/y} \\ S + H_2 + M \longrightarrow H_2S + M'. \end{cases}$$
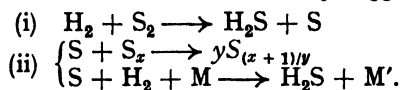
4. The work of Bodenstein and of Norrish and Rideal has been discussed.

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13. *2-Chloro-3 : 5-dinitro-4-chloromethyl- and 2 : 4 : 6-Tribromo-3-bromomethyl-benzoic Acids and Attempts to resolve them.*

By A. WEISSBERGER, H. BACH, and E. STRASSER.

THE existence of enantiomorphous molecules of certain derivatives of diphenyl, naphthalene, and similar compounds is due to steric interferences which block the rotation about a single bond (Mills, *Chem. and Ind.*, 1926, **45**, 884; Adams and Yuan, *Chem. Rev.*, 1933, **12**, 261). For the same reason, resolution would be expected with *mononuclear* compounds of the type (I), if differences between α and α' or a substituent in position 3 or 5 removes the symmetry about the 1 : 4 axis, and if the mutual transformation of (I*a*) and (I*b*) is sufficiently hindered by blocking of the rotation of β — γ about the link to the ring. Attempts to realise such cases have been described by Adams and his collaborators (*J. Amer. Chem. Soc.*, 1928, **50**, 2499; 1930, **52**, 2959; 1933, **55**, 4683) and by Le Fèvre (J., 1933, 977); no resolution, however, could be obtained.* We also were unsuccessful in our experiments, which we began from a somewhat different point of view before the publication of those papers.
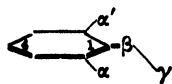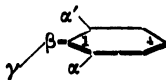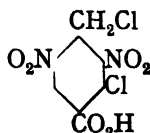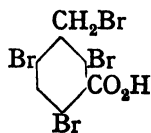
(I*a*.)   (I*b*.)   (II.)   (III.)

The possibility of resolving a compound of the type under discussion depends on two factors; in addition to the size and position of the groups or atoms α, α', and γ, the groups whose steric interference inhibits the change of (I*a*) into (I*b*), there must also be considered

* The possibility of resolving compounds of the type mentioned was in fact investigated in experiments carried out about 50 years ago, the object of which was to examine the constitution of the benzene skeleton (Le Bel, *Bull. Soc. chim.*, 1882, **38**, 98; Lewkowitsch, J., 1888, **53**, 781; V. Meyer, Lühn, and Sudborough, see Meyer–Jacobson, " Lehrbuch," II, 1, p. 63).

the ease with which the groups can slip past one another by distortion from their normal positions. Such distortion should be less probable the smaller the number of bonds involved, unless some special arrangement of the bonds causes a special rigidity. The fig. shows the position through which the molecule must pass for (I*a*) to become (I*b*), in the case of the simplest mononuclear aromatic system, all the atoms being taken as of the same size (and the angles those of the benzene nucleus and the regular tetrahedron). Obviously interference is to be expected only if the atoms involved are of greater volume, or *if they carry charges of the same sign*, where the electrical repulsion has the effect of increasing their apparent volume (Weissberger and Sängewald, *Physikal. Z.*, 1929, **30**, 792).

The first substance investigated was 2-chloro-3 : 5-dinitro-4-chloromethylbenzoic acid (II). The efforts to resolve this acid by means of salt formation with optically active bases in the usual way were unsuccessful. As it seemed possible that the acid after liberation from the base racemised too quickly to be detected in the active form, this result was controlled by comparison of the rotatory power of the salts themselves with the activity of the corresponding salts of 3-chloro-2 : 6-dinitro-*p*-toluic acid; no differences exceeding the limits of error were observed.

We next worked with 2 : 4 : 6-tribromo-3-bromomethylbenzoic acid (III). This would be expected to be more suitable because the substituent γ is bromine of slightly greater radius than chlorine, and because the groups α and α' are also bromine atoms. Unlike the nitro-group, the bromine atom, because of its higher symmetry, cannot turn out of the way of the interfering group by rotation about the bond to the nucleus, and further the electric field, which should increase its effective volume with respect to the interfering bromine atom of the methyl group, is homogeneous in all directions round the axis formed by the bond to the ring. Repulsion of a negatively charged atom by the nitro-group, however, would only be expected in a position where it is faced by an oxygen atom.
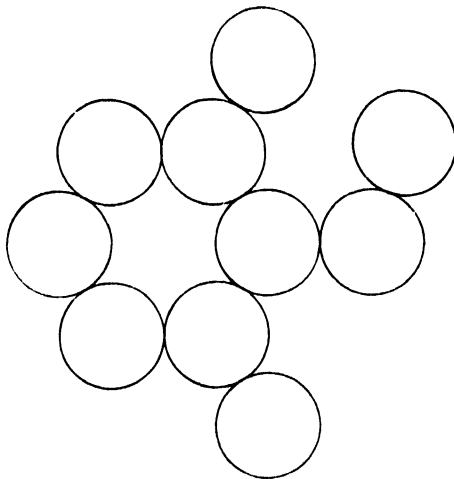
The attempts to resolve this acid—which contains the bromine atom in the *p*-position to the bromomethyl group because it is more easily prepared than the acid without it— with optically active bases were, however, a failure. No difference could be observed between the rotatory power of the salts, as far as these proved to be formed by salt formation of the carboxylic group, and those of the corresponding acid with no substituent in the methyl group. The conditions of salt formation needed care, since under some conditions the bromine atom in the side chain reacted more readily than the precipitation of the ordinary salt proceeded, even in solvents where the reactivity of this bromine atom would be expected to be small (Menschutkin, *Z. physikal. Chem.*, 1890, **6**, 41; Grimm, Ruff, and Wolff, *ibid.*, 1931, **B, 13**, 301). The carboxyl group seems to be markedly affected by the two bromine atoms in the *o*-positions to it.

Further investigation on the line pointed out in this paper should attempt another increase of α and of γ, the enclosure of the carboxyl or another reactive group between two substituents being avoided if possible.

EXPERIMENTAL.

3-Chloro-*p*-toluidine was prepared according to Blanksma (*Rec. trav. chim.*, 1906, **25**, 370). *p*-Nitrotoluene (350 g.), in boiling alcohol (1500 c.c.) and hydrochloric acid (3000 c.c., *d* 1·19), was reduced with stannous chloride (1700 g.) in hydrochloric acid (2000 c.c., *d* 1·19), added slowly. Boiling was continued for 1 hour, the mixture made alkaline, *p*-toluidine and 3-chloro-*p*-toluidine driven over by steam, transformed into the hydrochlorides (350 g.) and subjected to

steam-distillation. Only 3-chloro-*p*-toluidine went over; some which remained with the more basic *p*-toluidine also went over after addition of an amount of caustic soda equivalent to the base already driven out. Yield, 97 g. (26·8% of the theoretical), b. p. 225—226°, m. p. 6—7°.

3-Chloro-*p*-toluonitrile was prepared according to Claus and Davidsen (*J. pr. Chem.*, 1889, **39**, 491). 3-Chloro-*p*-toluidine (140 g.) in water (200 c.c.), hydrochloric acid (*d* 1·19, 400 c.c.), and ice (800 g.), was diazotised with sodium nitrite (70 g., in water, 230 c.c.). This solution was quickly added with mechanical stirring to a boiling cuprous cyanide mixture (prepared from 500 g. of copper sulphate; Henle, " Org. Chem. Prakt.," 2nd ed., 1927, p. 148), and boiling continued for 10 minutes. Steam-distillation, followed by recrystallisation from alcohol, yielded 90 g. (60%), m. p. 60—61°.

2-*Chloro-4-chloromethylbenzonitrile.*—3-Chloro-*p*-toluonitrile (20 g.) and phosphorus penta-chloride (30 g.) were heated for 5 hours in a large sealed tube at 200°; the mixture was then poured on ice, and the solid dried and recrystallised 5—7 times from light petroleum (b. p. 40—60°), giving 7·6 g. of colourless needles, m. p. 68—69·5° (Found : Cl, 38·1. $C_8H_5NCl_2$ requires Cl, 38·1%). The position of the newly introduced chlorine was proved by the produc-tion of chlorine ion on boiling with alcoholic potassium hydroxide solution; it was determined according to Schultze (*Ber.*, 1884, **17**, 1675) (Found : ionised Cl, 19·05; calc., 19·07%).

Treatment of fused 3-chloro-*p*-toluonitrile with chlorine in light was not a convenient method of preparation : a product, m. p. 67—69°, was isolated which contained three chlorine atoms.

5-*Chloro-2-nitro*-p-*toluonitrile.*—Treatment of 3-chloro-*p*-toluonitrile with nitration acid (2 parts of HNO_3, *d* 1·4, and 3 parts of H_2SO_4) for 30 minutes at 60° gave a neutral compound, m. p. 91·5—92·5° after recrystallisation from alcohol (Found : C, 49·05; H, 2·15; N, 14·1. Calc. : C, 48·9; H, 2·6; N, 14·3%). Yield, 90%. According to the analysis and m. p., and m. p. of the acid, 180°, obtained by saponification with 70% sulphuric acid, the compound is 5-chloro-2-nitro-*p*-toluonitrile, which was prepared by Claus and Davidsen (*Annalen*, 1891, **265**, 345) from 5-chloro-2-nitro-*p*-toluidine by the Sandmeyer reaction.

3-*Chloro-2 : 6-dinitro*-p-*toluic Acid.*—3-Chloro-*p*-toluonitrile (2 g.) was dissolved in concen-trated sulphuric acid (16 g.) and nitric acid (4 g., *d* 1·52) and heated in a water-bath. A violent reaction ensued and an acid was precipitated, m. p. 229—230·5° after recrystallisation from 60% alcohol and 235—237° after recrystallisation from xylene. The same substance was obtained by the corresponding treatment of 5-chloro-2-nitro-*p*-toluonitrile and is identical with that prepared by Claus and Davidsen (*loc. cit.*) by nitration of the corresponding acids.

2-*Chloro-3 : 5-dinitro-4-chloromethylbenzoic Acid.*—2-Chloro-4-chloromethylbenzonitrile (3·7 g.) was added to a mixture of concentrated sulphuric acid (30 g.) and nitric acid (7·5 g., *d* 1·52) and slowly heated in a water-bath. (The reaction sometimes goes on smoothly and is completed after a few minutes at 100°; sometimes, however, it becomes very violent and must be stopped by cooling.) The *dinitro-acid* was collected after cooling, washed with a little ice-water (yield, 3·7 g., m. p. 185—189°), and recrystallised three times from 25% alcohol, giving faintly yellow needles, m. p. 195—197°, 198—200° (corr.*) [Found : C, 32·3; H, 1·4; N, 9·6; Cl, 24·0; *M*, in dioxan (Weissberger and Bach, *J. pr. Chem.*, 1930, **127**, 262), 303. $C_8H_4O_6N_2Cl_2$ requires C, 32·5; H, 1·4; N, 9·5; Cl, 24·0%; *M*, 295]. The positions of the nitro-groups are obviously 3 : 5, since the substituents already present and the first entering nitro-group uniformly direct substituents into these positions and the entrance of two nitro-groups in *o*-positions to each other seems impossible under the conditions of preparation.

2 : 4 : 6-*Tribromo*-m-*toluonitrile.*—2 : 4 : 6-Tribromo-*m*-toluidine (68 g.) was dissolved in concentrated sulphuric acid (160 g.) and poured on ice to get it into an easily diazotisable form; most of the acid was then neutralised by addition, with cooling, of a solution of 80 g. of sodium hydroxide (80 g.) in water (200 c.c.). 2 Hours after diazotisation (sodium nitrite, 15 g., in water, 50 c.c.), the solution was filtered and dropped into a solution prepared from hydrated copper sulphate (70 g.), water (700 c.c.), and potassium cyanide (125 g.) at 90°. The precipitate was collected when cool, and extracted with boiling alcohol (2 × 400 c.c.). The alcoholic solutions were diluted with water (800 c.c.), whereupon the *nitrile* crystallised. Recrystallisation from ligroin gave 34 g. of colourless crystals, m. p. 122—123° (123—124°, corr.) after further recrystal-lisation from ligroin or *cyclo*hexane (Found : C, 27·0; H, 1·4; Br, 67·7. $C_8H_4NBr_3$ requires C, 27·1; H, 1·1; Br, 67·8%).

2 : 4 : 6-*Tribromo*-m-*toluamide.*—2 : 4 : 6-Tribromo-*m*-toluonitrile (8 g.) and 66% hydro-bromic acid (15 c.c.) were heated in a sealed tube for 14 hours at 160—180°. The product was filtered, washed with water, and triturated with dilute sodium hydroxide solution to remove

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* Corrected according to Berl and Kullmann, *Ber.*, 1927, **60**, 811.

the acid; on acidification, 2 : 4 : 6-tribromo-*m*-toluic acid (0·35 g.) separated. The residue was dried, extracted with light petroleum, which removed 2 : 4 : 6-tribromotoluene (0·1 g.), and recrystallised from 50% alcohol, giving 6·5 g. of colourless crystals, m. p. 199—200°, 202—203° (corr.) (Found : C, 26·0; H, 1·8; Br, 64·3. $C_8H_6ONBr_3$ requires C, 25·8; H, 1·6; Br, 64·5%). This method of saponification was used with regard to the eventual necessity of saponification of the nitrile brominated in the side chain.

2 : 4 : 6-*Tribromo*-m-*toluic* Acid.—To the amide (17 g.), dissolved in concentrated sulphuric acid (200 c.c.) and cooled with ice, a solution of sodium nitrite (15 g.) in water (40 c.c.) was added by means of a capillary which reached to the bottom of the bottle (Gattermann, *Ber.*, 1899, 32, 1118). The mixture was slowly heated to 90°, kept for 4 hours at this temperature, then poured on ice, and filtered. The residue was dissolved in 0·5*N*-sodium hydroxide, and the filtered solution treated with hydrochloric acid. The *acid* obtained separated from 50% methyl alcohol as colourless needles, sintering at about 160°, m. p. 187·5—188·5°, 190·5—191·5° (corr.). Investigation under the hot-stage microscope showed that the sintering is due to polymorphism (Found : C, 25·9; H, 1·6; Br, 64·1. $C_8H_5O_2Br_3$ requires C, 25·75; H, 1·3; Br, 64·3%).

2 : 4 : 6-*Tribromo*-3-*bromomethylbenzoic* Acid.—The introduction of bromine into the methyl group was carried out according to Helferich and Gootz (*Ber.*, 1932, 65, 407). 2 : 4 : 6-Tribromo-*m*-toluic acid (13·3 g.) was dissolved in alcohol-free chloroform (350 c.c.), finely powdered sodium bicarbonate (3 g.) added, and then a solution of bromine (5·9 g.) in chloroform (50 c.c.). This mixture was mechanically stirred and, the outside of the bottle being cooled by a stream of air, insolated with a 500 watt lamp till it was colourless. After evaporation of the chloroform the residue was recrystallised from benzene, yielding 12·2 g. (76%) of colourless needles, m. p. 180·5—181·5°, 183·5—184·5° (corr.). This *acid* too is polymorphous; faint sintering occurs at about 160° and a sample introduced into the melting-point apparatus at 175° melted completely, but solidified after a short time at the same temperature and then exhibited the melting point noted above (Found : C, 21·6; H, 1·1; Br, 70·5. $C_8H_4O_2Br_4$ requires C, 21·6; H, 0·9; Br, 70·8%).

Attempted Resolutions.—The salts of 2-chloro-3 : 5-dinitro-4-chloromethylbenzoic acid with brucine, in alcohol and alcohol–chloroform, strychnine, quinine, and quinidine, in alcohol, were prepared by mixing solutions of equivalent amounts of the acid and the base in such concentrations that about one half of the salts crystallised on standing. These crystallisates showed, in chloroform or in acetone solution, no other activities than the corresponding salts of the 3-chloro-2 : 6-dinitro-*p*-toluic acid.

The salt of 2 : 4 : 6-tribromo-3-bromomethylbenzoic acid with brucine which was quickly precipitated (about one half of the total) from acetone or benzene solution on scratching showed no other rotatory power, in chloroform, than that of 2 : 4 : 6-tribromo-*m*-toluic acid. From alcohol, the whole of the salt was precipitated, either quickly on scratching or slowly without; it also showed no different activity. If the crystallisation from acetone, benzene, or dioxan proceeded slowly, the precipitates exhibited other (positive) rotatory powers. They proved to be hydrobromides of bases which were formed by condensation involving the bromomethyl group and could not be decomposed by shaking with acid under conditions where the salts with the same rotatory powers as those of the acid with no bromine in the side chain were decomposed. This decomposition also required a rather long treatment; obviously the decomposition of the salts is hindered by the proximity of the bromines to the carboxyl group.

Corresponding observations were made with coniine (in ether, amyl ether and acetone), quinine (in acetone, alcohol, benzene), and morphine (in acetone, alcohol–acetone and dioxan-acetone), at the ordinary and at low temperatures (freezing mixture, carbon dioxide snow).

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14. *The Action of Aromatic Aldehydes on Benzene and Toluene in Presence of Aluminium Chloride.*

By Donald H. Hey.

Gattermann and Koch's method (*Ber.*, 1897, **30**, 1622) for the synthesis of aromatic aldehydes, namely, the action of a mixture of hydrogen chloride and carbon monoxide on a homologue of benzene in presence of aluminium and cuprous chlorides, is stated to be inapplicable to benzene itself (Gattermann and Koch, *loc. cit.*; Gattermann, *Annalen*, 1906, **347**, 347). Benzene is therefore recommended as a solvent or diluent for the reaction in place of carbon disulphide, which, since it does not dissolve the cuprous chloride, tends to inhibit the reaction. The product obtained by this method from diphenyl in benzene solution (J., 1931, 2477) contained, however, benzaldehyde in addition to diphenyl-4-aldehyde; and in a reaction carried out on benzene alone, at 45°, benzaldehyde was formed together with a small quantity of anthracene.

Benzene does not react with hydrogen cyanide and hydrogen chloride in the presence of aluminium chloride at 40° (Gattermann and co-workers, *Ber.*, 1898, **31**, 1149, 1765), but at a higher temperature a considerable quantity of benzaldehyde is formed (Hinkel, Ayling, and Morgan, J., 1932, 2793). The formation of benzaldehyde from benzene in the carbon monoxide reaction is therefore not unexpected, especially since it is known that benzaldehyde is readily formed when aluminium bromide is used in place of the chloride. Further, in presence of aluminium chloride, aldehydes are formed from aromatic hydrocarbons, including benzene, and carbon monoxide under pressure (Boehringer, D.R.-P. 1914, 281,212; Longman, *J. Soc. Chem. Ind.*, 1916, **35**, 384; B.P. 1915, 3152; see also Holloway and Krase, *Ind. Eng. Chem.*, 1933, **25**, 497) and from benzene and toluene reacting with nickel carbonyl (Dewar and Jones, J., 1904, **85**, 212). The interaction of benzaldehyde with benzene in presence of aluminium chloride with formation of anthracene (Schaarschmidt, Hermann, and Szemzö, *Ber.*, 1925, **58**, 1914) may partly account for the inability of Gattermann and his co-workers to observe the formation of the aldehyde from benzene.

To elucidate the formation of anthracene in this reaction, experiments were carried out with toluene in place of benzene, and with methyl- and chloro-benzaldehydes replacing benzaldehyde. The action of benzaldehyde on benzene in presence of aluminium chloride at 60° gave, as recorded by Schaarschmidt, Hermann, and Szemzö (*loc. cit.*), anthracene and triphenylmethane, but with toluene in place of benzene a mixture of 2 : 6- and 2 : 7-dimethylanthracene was obtained—a further example of the production together of these two isomerides (see Lavaux, *Compt. rend.*, 1904, **139**, 976; 1905, **140**, 44; **141**, 204, 354; 1906, **143**, 687; 1908, **146**, 135, 345; 1911, **152**, 1400; *Ann. Chim.*, 1910, **20**, 433; **21**, 131). Lavaux showed that the mixture behaved as a chemical entity with a sharp melting point, but, although a separation into the two isomerides was effected, the constitutions originally assigned to them have been since shown by Morgan and Coulson (J., 1929, 2203) to be at fault.

On the other hand, when *m*-tolualdehyde, *p*-tolualdehyde, or *o*-chlorobenzaldehyde reacted with benzene in presence of aluminium chloride, the product consisted of anthracene and triphenylmethane, together with toluene and *m*-xylene (from the tolualdehydes) and chlorobenzene (from *o*-chlorobenzaldehyde).

From these results it must be inferred (*a*) that it is the hydrocarbon nuclei alone which go to form the two end-rings in the anthracene molecule and the three rings in triphenylmethane, and (*b*) that the aldehyde supplies the *meso*-carbon atoms in the anthracene molecule and the methane carbon atom in triphenylmethane. The formation of a triaryl-methane by elimination of water from one molecule of aldehyde and two molecules of hydrocarbon, as has been shown to take place between benzaldehyde and benzene or toluene in presence of zinc chloride at a high temperature (Griepentrog, *Ber.*, 1886, **19**, 1876; cf. Kliegl, *Ber.*, 1905, **38**, 85), does not occur.

The formation of toluene, *m*-xylene, and chlorobenzene (above) would indicate that the carbonyl group is severed from the aldehyde, and this would imply the reversibility of the reaction between benzene and carbon monoxide, thus $C_6H_5 \cdot CHO \rightleftharpoons C_6H_6 + CO$.

In order to test this possibility the action of aluminium chloride on benzaldehyde alone was studied and it was found that much heat was evolved, together with a water-insoluble gas which burned with the characteristic blue flame of carbon monoxide and was capable of oxidation to carbon dioxide. Further, when carbon monoxide was passed into hot toluene containing aluminium chloride, a mixture of 2 : 6- and 2 : 7-dimethylanthracene was formed, together with a liquid product probably consisting of a mixture of tritolylmethanes.* The action of furfuraldehyde on toluene in presence of aluminium chloride also gave the mixture of dimethylanthracenes, thus further confirming the fact that the nucleus to which the aldehyde group is attached plays no part in the building up of the anthracene molecule. The experiments of Frankforter and Kokatnur (*J. Amer. Chem. Soc.*, 1914, **36**, 1529), who condensed trioxymethylene with benzene and with toluene in presence of aluminium chloride, also support this view : in the former case anthracene was obtained, and in the latter dimethylanthracene, which, however, was not separated into the two possible iso- merides. The formation of anthracene from benzene and of dimethylanthracene from toluene, in presence of nickel carbonyl and aluminium chloride at 100°, as demonstrated by Dewar and Jones (*loc. cit.*), is also in agreement with the view now proffered, but the mechanism suggested by these authors, involving the aromatic aldehyde as an essential intermediate, is no longer tenable. This mechanism has been previously rejected by Morgan and Coulson (*loc. cit.*) on other grounds.

The main inferences drawn with regard to the mechanism of the building of the anthracene and triphenylmethane molecules, in the reaction between the aldehyde and the aromatic hydrocarbon in presence of aluminium chloride, are thus clearly substantiated. It is obvious, however, that several minor reactions may also occur in presence of the aluminium chloride, *e.g.*, the conversion of triphenylmethane into diphenylmethane, benzene, and anthracene (Friedel and Crafts, *Ann. Chim.*, 1884, **1**, 492; Scholl and Seer, *Ber.*, 1922, **55**, 335), the transference of methyl groups, and also the pyrogenic-like fission of the aromatic nuclei.

<div align="center">EXPERIMENTAL.</div>

Action of Carbon Monoxide and Hydrogen Chloride on Benzene in Presence of Aluminium and Cuprous Chlorides.—A stream of dry carbon monoxide and hydrogen chloride was passed for 7 hours into a well-stirred mixture of benzene (200 g.), aluminium chloride (100 g.), and cuprous chloride (15 g.) at 45°. The product was poured on ice and distilled with steam. The benzene layer in the distillate was separated, the aqueous layer extracted with more benzene, and the combined benzene extracts dried and distilled, giving, after removal of the benzene, a fraction, b. p. 175—182°, consisting almost wholly of benzaldehyde (8·5 g.), and a small residue of benzoic acid. The solid non-steam-volatile residue was digested with hot absolute alcohol, from which a yellow crystalline solid (0·75 g.) separated on cooling. Recrystallisation from absolute alcohol gave anthracene in white flakes (m. p. and mixed m. p. 212—213°). The picrate separated from alcohol in red needles (m. p. and mixed m. p. 141—142°).

Action of Benzaldehyde on Toluene in Presence of Aluminium Chloride.—Benzaldehyde (53 g.) was added slowly to a mixture of toluene (160 g.) and aluminium chloride (150 g.). The mixture, which darkened and became warm, was stirred for 6 hours at 60°. The product was poured on ice and distilled with steam. Toluene and benzaldehyde (12 g.) were collected in the distillate, together with a small quantity of a mixture of 2 : 6- and 2 : 7-dimethylanthracene (m. p. 219—220°). The non-steam-volatile residue yielded a yellow solid (34 g.) on distillation, which after crystallisation from toluene gave a mixture of 2 : 6- and 2 : 7-dimethylanthracene, m. p. 221—222° (Found : C, 92·9; H, 6·5. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). On treatment with concentrated sulphuric acid and a trace of nitric acid, a deep purple coloration was obtained (cf. Dewar and Jones, J., 1904, **85**, 216). No monomethylanthracene could be detected in the product. A portion of the mixture of dimethylanthracenes (11 g.) was oxidised in boiling glacial acetic acid with a concentrated solution of chromic anhydride (15 g.) in water. After ½ hour the green solution was poured into water, which precipitated the mixture of dimethylanthraquinones (12 g., m. p. 155—170°). This mixture, after several crystallisations from absolute alcohol, gave mainly 2 : 6-dimethylanthraquinone (m. p. 234—236° after recrystallisation from glacial acetic acid), and a smaller quantity of 2 : 7-dimethylanthraquinone (m. p. 159—160°) was obtained

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* Anschütz and Immendorff (*Ber.*, 1884, **17**, 2816; 1885, **18**, 657) have shown that the action of aluminium chloride on boiling toluene alone produces some dimethylanthracene, but the yield in this case is only minute (cf. Lavaux, *Ann. Chim.*, 1910, **20**, 468).

from the mother-liquors. The identity of the two dimethylanthraquinones was proved by means of mixed melting points with the corresponding compounds prepared by oxidation of the mixture of hydrocarbons obtained by the method of Lavaux from toluene, methylene dichloride, and aluminium chloride (*Compt. rend.*, 1905, **140**, 44), a reaction which has been shown by Morgan and Coulson (J., 1929, 2212) to give rise to a mixture of 2 : 6- and 2 : 7-dimethylanthracene. The mixture of the two hydrocarbons thus obtained melted at 224°, and did not depress the melting point of the product prepared from benzaldehyde, toluene, and aluminium chloride. Oxidation with chromic anhydride and subsequent fractionation by crystallisation from absolute alcohol gave mainly 2 : 7-dimethylanthraquinone (m. p. 160—162°), together with a smaller quantity of 2 : 6-dimethylanthraquinone (m. p. 232—234°).

Action of p-Tolualdehyde on Benzene in Presence of Aluminium Chloride.—*p*-Tolualdehyde (25 g.) was added gradually to a well-stirred mixture of benzene (150 c.c.) and aluminium chloride (75 g.), which was kept at 60° for 6 hours; hydrogen chloride was freely evolved. After standing for 12 hours, the mixture was poured on ice, and distilled with steam until white fluorescent crystals of anthracene began to collect in the condenser. The dark brown solid residue was digested with hot absolute alcohol : anthracene (4 g.) separated from the filtrate, and sublimation of the insoluble residue (7 g.) also gave anthracene in white flakes (m. p. and mixed m. p. 212—213°). Oxidation with chromic anhydride and acetic acid gave anthraquinone (m. p. and mixed m. p. 276—277°, after crystallisation from acetic acid). Four successive fractions of crude anthracene separated from the alcoholic filtrate, but no evidence could be obtained of the presence of any mono- or di-methylanthracene. A portion of the residue from the alcoholic mother-liquor was distilled and collected mainly between 340° and 360°. This fraction solidified on cooling, and crystallisation from alcohol gave triphenylmethane (m. p. and mixed m. p. 90—92°). A second portion of the residue was oxidised in glacial acetic acid with chromic anhydride (¼ hour's boiling) : the product precipitated by water was removed, and ether extracted *p*-toluic and terephthalic acids from the filtrate. The precipitated product was dissolved in glacial acetic acid, from which a little anthraquinone separated. The mother-liquor, evaporated almost to dryness and triturated with cold absolute alcohol, deposited a crystalline solid, which was recrystallised from hot absolute alcohol. After the separation of a further small quantity of anthraquinone, colourless crystals were deposited, which after a further crystallisation from aqueous alcohol melted at 159—160°, both alone and on admixture with triphenylcarbinol (Found : C, 86·8; H, 6·0. Calc. for $C_{19}H_{16}O$: C, 87·6; H, 6·15%).

The benzene layer in the steam distillate was heated on the steam-bath to remove benzene, and further distillation gave a small colourless fraction (b. p. 110—130°) and finally unchanged *p*-tolualdehyde (6 g.). The former was nitrated by warming on the water-bath with an equi-volume mixture of concentrated sulphuric and fuming nitric acids. The nitration product was precipitated by the addition of water, and crystallisation from benzene gave fine, pale yellow needles, m. p. 180° alone or mixed with trinitro-*m*-xylene (Found : C, 40·3; H, 2·95; N, 17·4. Calc. for $C_8H_7O_6N_3$: C, 39·8; H, 2·9; N, 17·4%). A small quantity of *m*-dinitrobenzene separated from the mother-liquor.

Action of m-Tolualdehyde on Benzene in Presence of Aluminium Chloride.—The product from the reaction between *m*-tolualdehyde (23 g.), benzene (150 c.c.), and aluminium chloride (75 g.), carried out as described for *p*-tolualdehyde, was poured on ice and distilled with steam. The dark brown non-volatile residue was digested with hot absolute alcohol and filtered. Several crops of crude anthracene (7 g.) separated from the filtrate, and sublimation of the insoluble residue (9 g.) also gave anthracene. No methylanthracenes could be detected in the product. The alcoholic mother-liquor was finally distilled and a main fraction, b. p. 340—360°, was collected which solidified when cold. Crystallisation from absolute alcohol gave triphenyl-methane (m. p. and mixed m. p. 89—91°).

The benzene layer in the steam distillate was dried and distilled with a Dufton column. Three fractions were collected, (i) b. p. 80—95°, (ii) b. p. 110—115°, and (iii) b. p. 135—145°, leaving a small residue boiling above 145° and consisting mainly of unchanged *m*-tolualdehyde. Fractions (ii) and (iii) were each nitrated by warming on the water-bath with concentrated sulphuric and fuming nitric acids, and the products were precipitated by water. From fraction (ii), 2 : 4-dinitrotoluene was obtained in pale yellow needles, m. p. 70—71° (after two crystallis-ations from alcohol), both alone and on admixture with an authentic specimen. The product from fraction (iii) was washed with hot alcohol, and crystallisation from benzene gave trinitro-*m*-xylene in yellow needles, m. p. and mixed m. p. 179—181°.

Action of o-Chlorobenzaldehyde on Benzene in Presence of Aluminium Chloride.—The reaction between *o*-chlorobenzaldehyde (25 g.), benzene (150 c.c.), and aluminium chloride (75 g.) was carried out in the manner previously described, and the product was poured on ice and distilled

with steam. The non-volatile residue was digested with hot absolute alcohol and filtered. The residue (6 g.) was heated with a mixture of toluene and glacial acetic acid and, after filtration, anthracene separated from the solution (m. p. and mixed m. p. 212—213°, after recrystallisation). The alcoholic filtrate also deposited anthracene (7 g.), and finally the mother-liquor was distilled and gave a dark oil (b. p. 340—355°, 11 g.), which solidified. Recrystallisation of the latter from alcohol gave triphenylmethane, m. p. and mixed m. p. 90—91° (Found : C, 93·4; H, 6·5. Calc. for $C_{19}H_{16}$: C, 93·4; H, 6·6%). The benzene layer in the steam distillate was separated, and the benzene removed on the steam-bath. The residual liquid, on distillation with a Dufton column, gave one main fraction (8·1 g.), b. p. 130—133°, which was identified as chlorobenzene (*a*) by nitration with fuming nitric acid to give *p*-chloronitrobenzene (m. p. and mixed m. p. 83—84°; piperidino-derivative, m. p. 76—77°), and (*b*) by nitration with fuming nitric and concentrated sulphuric acids to give 2 : 4-dinitrochlorobenzene (m. p. 46°), which on warming with aniline gave 2 : 4-dinitrodiphenylamine (m. p. 156°).

Action of Furfuraldehyde on Toluene in Presence of Aluminium Chloride.—Furfuraldehyde (32 g.) was added gradually to a well-stirred mixture of toluene (110 c.c.) and aluminium chloride (100 g.), and the mixture was kept at 60° for 6 hours; evolution of hydrogen chloride occurred. After standing for 12 hours, the mixture set to a stiff black paste, which was transferred to ice and distilled with steam. The non-steam-volatile residue set to a solid black brittle mass (96 g.), which was distilled in portions and yielded a dark viscous oil (48 g., b. p. 300—420°). This was subsequently redistilled and collected in four fractions, (i) 5 g., b. p. 280—320°, (ii) 9 g., b. p. 320—360°, (iii) 10·5 g., b. p. 360—400°, and (iv) 12 g., b. p. 400—430°. Fractions (i), (ii), and (iii) deposited crystalline precipitates of dimethylanthracenes on standing, which were filtered off and recrystallised from toluene (m. p. and mixed m. p. 221—222°; 4 g.). Difficulty was experienced in isolating further quantities of dimethylanthracenes owing to their contamination with an excessive quantity of a viscous oily by-product.

Action of Carbon Monoxide and Hydrogen Chloride on Boiling Toluene in Presence of Aluminium Chloride.—A steady stream of dry carbon monoxide and hydrogen chloride was passed for 6 hours into boiling toluene (150 c.c.) in presence of aluminium chloride (75 g.). After standing for 12 hours, the dark viscous fluid was poured on ice and distilled with steam. The toluene layer in the steam distillate was separated and distillation gave three fractions, (i) b. p. 90—165° (62 c.c., recovered hydrocarbons), (ii) b. p. 170—200° (3 c.c.), and (iii) b. p. 200—230° (3 c.c.). Fractions (ii) and (iii), consisting of colourless clear oils, were treated together with an excess of warm aqueous potassium permanganate, but only a small portion was oxidisable. After saturation with sulphur dioxide, ether was added, and the aqueous layer drawn off. The ethereal layer was washed with aqueous sodium hydroxide, and acidification of the alkaline washings gave a minute precipitate only. Evaporation of the dried ethereal extract left an oil, which would not de-colorise potassium permanganate but reacted readily with 2 : 4-dinitrophenylhydrazine, giving a 2 : 4-dinitrophenylhydrazone, which separated from absolute alcohol in crimson needles, m. p. 245° (decomp.). The non-steam-volatile viscous residue was extracted with hot toluene and distilled. After removal of the solvent, two fractions were collected, (i) b. p. 200—290° (3·5 g.), and (ii) b. p. 290—380° (36 g.). The latter consisted of a dark red oil, which on trituration with benzene slowly deposited a mixture of 2 : 6- and 2 : 7-dimethylanthracene (5 g., m. p. 220—221°). The residual oil, which would not solidify, probably consisted mainly of a mixture of tritolyl-methanes from which the further separation of dimethylanthracene was difficult.

Action of Aluminium Chloride on Benzaldehyde.—(*a*) On adding benzaldehyde to powdered aluminium chloride, considerable heat was developed and some hydrogen chloride was evolved. The evolved gases were passed through a wash-bottle containing water and then collected over water. The gas thus collected burned with a blue flame.

(*b*) A slow stream of nitrogen was passed over a mixture of benzaldehyde (200 g.) and aluminium chloride (100 g.) at 60—70° and then successively through a trap cooled in ice, a bulb containing water, a soda–lime tube, a potash bulb, a bulb containing baryta water (B_1), a tube containing heated copper oxide, a second bulb containing baryta water (B_2), and finally a soda–lime tube. The baryta water in the bulb B_1 remained clear, whereas that in B_2 soon became cloudy and deposited a precipitate of barium carbonate. No products were evolved which could be condensed at 0°. The mixture of benzaldehyde and aluminium chloride became viscous and finally set to a solid black mass when cold. Steam distillation of this product gave benzaldehyde (150 g.) and a non-volatile buff amorphous solid (27 g.), insoluble in alcohol, containing aluminium but no chlorine, and from which benzaldehyde and benzoic acid were liberated on treatment with aqueous alkali or acid.

THE UNIVERSITY, MANCHESTER.

15. *Light Filters for the Mercury Lamp.*

By E. J. Bowen.

THE following filters are an improvement on a previous list (Bowen, J., 1932, 2236) and have been found useful for photochemical work with the mercury lamp, from which a concentrated beam of light may be obtained by placing the filter of col. 2 of the table in a round flask (glass for the visible region and the 3660 Å. line, silica for the ultra-violet) of 10 cm. diameter (and 500 c.c. capacity) very near the lamp, followed by the other filters, the reaction cell being placed behind a diaphragm about 24 cm. from the lamp.

The nickel–cobalt sulphate filter, which transmits the ultra-violet while practically cutting off all the visible, infra-red, and the 3660 Å. line, is similar to that recommended by Bäckström (*Naturwiss.*, 1933, **13**, 251), and must be particularly free from traces of iron salts. Salts of " Analar " standard (B.D.H. and Messrs. Hopkin and Williams, Ltd.) have been found suitable.

Mercury lines, Å.						
2480 2540	145 g. $NiSO_4,6—7H_2O$ + 41·5 g. $CoSO_4,7H_2O$ in 1 l. water; 10 cm.	Gaseous Cl_2 at 1 atm.; 3 cm.	0·108 g. I_2 + † 0·155 g. KI in 1 l. water; 1 cm.			
2650 2700			CCl_4, 2 mm.; † *or* $HgCl_2$ * (45 g./l.) in water, 1 cm.			
2750 2805						
2895 2925 2970 3030						Oxalic acid † soln. in water (20 g./l.); 1 cm. Or $CuSO_4,5H_2O$ in water (15 g./l.); 1 cm.
3135				Potassium † hydrogen phthalate, 5 g./l. in water; 1 cm.		
3340			Uric † acid, satd. soln. in water; 1 cm.			
3660	4·4 g. $CuSO_4,5H_2O$ + 150 c.c. NH_4OH (*d* 0·88) in 1 l. water; 10 cm.		2—3 mm. Chance's black " ultra-violet " glass.			
4050			I_2 in CCl_4 (7·5 g./l.), 1 cm. + quinine hydrochloride in water † (10 g./l.), 2 cm.			
4360			75 g. $NaNO_2$ in 100 c.c. water; * 1 cm.			
5460	13 g. $CuSO_4,5H_2O$ + 0·44 g. $K_2Cr_2O_7$ + 50 c.c. conc. H_2SO_4 in 1 l. water; 10 cm.		Corning glass 512, 5 mm.			
5770 5790			Corning glass 344, 3·4 mm.			

* Renew occasionally.   † Renew frequently.

UNIVERSITY COLLEGE, OXFORD.

16. *Homologues of Naphthacene. Part II. 2-Methyl- and 2:7-Dimethyl-naphthacene : Synthetic Applications of 2:6- and -2:7-Dimethyl-1:2:3:4-tetrahydronaphthalene.*

By EDWARD A. COULSON.

THE method used in synthesising 2:6-dimethylnaphthacene (J., 1934, 1406) becomes less effective when similar attempts are made to obtain 2-methyl- and 2:7-dimethyl-naphthacene. It had already been observed that the condensation of 2:6-dimethyl-3-naphthoyl chloride with benzene or toluene gave only poor yields, as in the formation of 3-*p*-toluoyl-2:6-dimethylnaphthalene from the latter hydrocarbon. But with 3:6-dimethyl-2-naphthoyl chloride similar condensations led to ill-defined and resinous products to such an extent as to impair the synthetical method.

A way out of the present difficulties was found in the preparation and use in Friedel-Crafts condensations of the tetrahydro-derivatives of 2:6- and 2:7-dimethylnaphthalene. Not only did these react as smoothly and quantitatively as benzene derivatives with acyl chlorides, but the products were homogeneous and of the expected type. A further and immediate advantage, leading to the ultimate synthesis of *linear* hydrocarbons, is that condensation is effected in the β-position. The tetrahydro-derivatives of 2:6- and 2:7-dimethylnaphthalene, which are readily obtained by hydrogenation, will probably be found to have many similar useful synthetical applications.

(I) 2:7-*Dimethylnaphthacene.*—3:6-*Dimethyl-2-naphthylamine*, obtained by the Bucherer reaction from the corresponding 3:6-dimethyl-2-naphthol (I), furnished 3:6-*dimethyl-2-naphthoic acid* (II) through its nitrile.
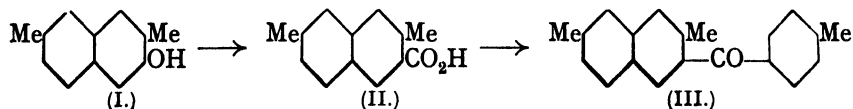
But when 3:6-*dimethyl-2-naphthoyl chloride* was treated with either benzene or toluene and aluminium chloride, there resulted resinous products from which the required ketones could not be crystallised. Nor could a pure product be isolated from the interaction of 2:6-dimethyl-3-naphthoyl chloride and benzene. The acyl chlorides appear to react upon themselves, rather than with the hydrocarbon. Incomplete condensation was brought about when ferric chloride, in place of aluminium chloride, was used as condensing agent, in the reaction between 3:6-dimethyl-2-naphthoyl chloride and toluene; and although much 3:6-dimethyl-2-naphthoic acid was recovered there was only a small yield of 2-*p*-toluoyl-3:6-dimethylnaphthalene (III), along with resinous products. This ketone charred on pyrolysis, but a small amount of 2:7-*dimethylnaphthacene* sublimed out of the charred residue and oxidised to the corresponding 9:10-*quinone*.
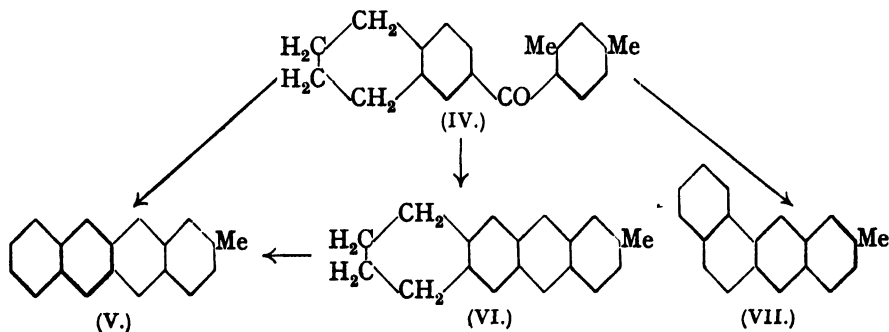
(II) 2-*Methylnaphthacene.*—When 6-(2':4'-*dimethyl*)*benzoyl*-1:2:3:4-*tetrahydro-naphthalene* (IV), obtained by condensing either 2:4-dimethylbenzoyl chloride with tetralin, or *m*-xylene with 1:2:3:4-tetrahydro-6-naphthoyl chloride, was heated to 400°,

it slowly lost water and hydrogen, furnishing a mixture of three hydrocarbons : 2-methyl-naphthacene (V), 6-methyl-1 : 2 : 3 : 4-tetrahydronaphthacene (VI), and 7-methyl-1 : 2-benzanthracene (VII). The first, a golden-orange substance of sparing solubility and high melting point, was easily separated from the mixture by fractional crystallisation. The residue containing the two last-mentioned compounds (which were less coloured but more fusible and soluble than the 2-methylnaphthacene) was dehydrogenated by heating with selenium, yielding a mixture readily separable into 2-methylnaphthacene and 7-methyl-1 : 2-benzanthracene.

(III) 2 : 6- *and* 2 : 7-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene : Supplementary Syntheses of Naphthacene Homologues.*—By hydrogenation of 2 : 7-dimethylnaphthalene with a molybdenum catalyst prepared as described by Hall (*Fuel*, 1933, **12**, 79) there may be obtained liquid products containing both 2 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (VIII) and 2 : 7-*dimethyldecahydronaphthalenes*. After heating for 4 hours at 300° with an initial pressure of 100 atmospheres of hydrogen, the product contained 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 237°, and unchanged 2 : 7-dimethylnaphthalene, b. p. 265° ; but when the temperature was raised to 390°, appreciable amounts of 2 : 7-dimethyldecahydronaphthalene, b. p. 216°, were formed and little or no 2 : 7-dimethyl-naphthalene was unchanged.

Smooth and quantitative condensation of 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydro-naphthalene with benzoyl and *p*-toluoyl chlorides occurs under the influence of aluminium chloride, the products being 6-*benzoyl*- and 6-p-*toluoyl*-2 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro-naphthalene* (IX ; R = H, CH₃). When these ketones are boiled, they yield as main products 2-*methyl*- and 2 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthacene* (X ; R = H, CH₃), but there are also formed smaller amounts of 2-methyl- and 2 : 7-dimethyl-naphthacene (XI ; R = H, CH₃).
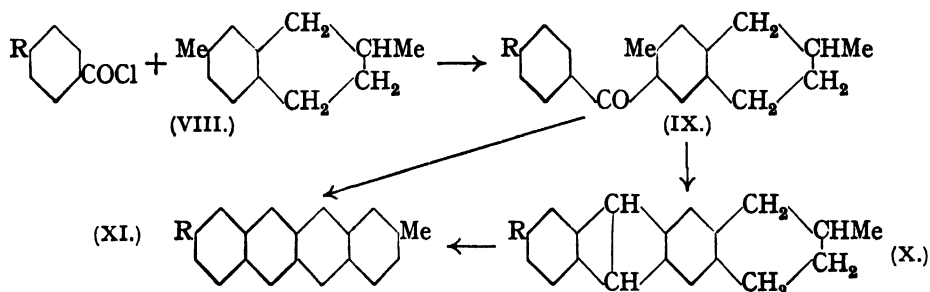
In each case dehydrogenation of the tetrahydronaphthacene derivative is readily brought about by heating with selenium at 240°.

That the initial ketone has the indicated structure is shown by the ultimate production of a *linear* 4-ring hydrocarbon, but there is further evidence that the hydrogen atom in the 6-position in 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene is, as would be expected, the most reactive. When treated with diphenylcarbamyl chloride, the hydrocarbon yields a *dimethyltetrahydronaphthodiphenylamide*, which when saponified gives the corresponding *acid*. The latter when dehydrogenated gives 3 : 6-dimethyl-2-naphthoic acid, identical with an authentic specimen, thus establishing the structure of the diphenylamide.

Sulphonation of 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene in the cold gives a good yield of a homogeneous monosulphonic acid, of which the structure is shown by its conversion, on caustic potash fusion, into a mixture containing both the corresponding 2 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-6-*naphthol* and 3 : 6-dimethyl-2-naphthol (compared with an authentic specimen).

Hydrogenation of 2 : 6-dimethylnaphthalene was effected by heating to 390° with hydrogen (initial pressure, 100 atmospheres) and the same catalyst as in the case of the 2 : 7-isomeride. The product contained both 2 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* and 2 : 6-*dimethyldecahydronaphthalene*. At 300°, little or no hydrogenation took place,

from which it seems that 2 : 6-dimethylnaphthalene requires a higher temperature than the 2 : 7-isomeride before hydrogenation begins.

Condensation was effected between 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene and *p*-toluoyl chloride and the resulting 7-*p*-*toluoyl*-2 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro-naphthalene* pyrolysed to yield both 2 : 6-dimethylnaphthacene and 2 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthacene*; the second was transformed into the first by heating with selenium. Experiments parallel to those with the 2 : 7-isomeride showed that in 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene the hydrogen atom in the 7-position was the most reactive. Two points of difference between the isomerides may be mentioned ; derivatives of 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene are less readily dehydrogenated ; and although both 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydro-7-naphthol and 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydro-6-naphthol have " wetting-out " properties, the first-mentioned appears by a conventional test to be very much superior to the latter.

EXPERIMENTAL.

3 : 6-*Dimethyl-2-naphthylamine.*—3 : 6-Dimethyl-2-naphthol was prepared from 2 : 7-dimethylnaphthalene through 2 : 7-dimethylnaphthalene-3-sulphonic acid as described by Weissgerber and Kruber (*Ber.*, 1919, **52**, 340). The naphthol (38 g.) was heated at 200° for 6 hours with 30 g. of ammonium sulphite and 400 c.c. of ammonia solution (*d* 0·880) in an autoclave, and the reaction product treated with excess of boiling dilute caustic soda solution, cooled, and extracted with ether. The crude hydrochloride of the base (30 g. ; 65% of the theoretical yield) was precipitated when the ethereal extract was shaken with 10% hydrochloric acid. Unchanged naphthol (11·0 g.) was recovered from the aqueous alkaline solution. 3 : 6-*Dimethyl-2-naphthylamine*, obtained by digestion of the hydrochloride with warm dilute caustic soda, was readily soluble in alcohol or benzene ; it crystallised from petroleum (b. p. 60—80°) in plates with satin-like sheen, m. p. 139° (Found : C, 84·2 ; H, 7·6. $C_{12}H_{13}N$ requires C, 84·2 ; H, 7·6%). The *hydrochloride*, colourless flakes, m. p. 283° (decomp.), is somewhat soluble in dilute hydrochloric acid (Found : Cl, 17·1. $C_{12}H_{13}N,HCl$ requires Cl, 17·1%). The *acetyl* derivative, m. p. 207°, separates from acetic acid or alcohol in tufts of colourless needles (Found : C, 78·9 ; H, 6·9. $C_{14}H_{15}ON$ requires C, 78·9 ; H, 7·0%).

3 : 6-*Dimethyl-2-naphthonitrile.*—The base (16·5 g.), suspended in 25 c.c. of concentrated hydrochloric acid and 80 c.c. of water, was diazotised at 0—5° with 8·0 g. of sodium nitrite, and the diazo-solution added to a cold Sandmeyer reagent, in a 4 l. flask, made from 34 g. of potassium cyanide, 30 g. of copper sulphate, and 160 c.c. of water. There was much effervescence when the first-formed precipitate was warmed to 100° and a suspension of the crude nitrile (11·0 g.) remained. Purified by sublimation and crystallisation from alcohol, 3 : 6-*dimethyl-2-naphtho-nitrile* formed tufts of colourless plates, m. p. 145° (Found : C, 86·0 ; H, 6·0. $C_{13}H_{11}N$ requires C, 86·2 ; H, 6·1%).

3 : 6-*Dimethyl-2-naphthoic Acid.*—The nitrile (from 16·5 g. of base) was heated with 50% caustic potash solution and alcohol for 24 hours. After dilution the solution was cooled and filtered, and the filtrate acidified, whereupon 3 : 6-*dimethyl-2-naphthoic acid* (11·0 g.) was precipitated. The acid crystallised from aqueous acetic acid in pale cream needles, m. p. 224°, sparingly soluble in water and soluble in acetic acid, alcohol, or benzene (Found : C, 77·9 ; H, 6·0. $C_{13}H_{12}O_2$ requires C, 78·0 ; H, 6·0%).

3 : 6-*Dimethyl-2-naphthoyl chloride*, obtained in almost theoretical yield by refluxing the acid for 2 hours with 3 times its weight of thionyl chloride, was purified by fractional distillation in a vacuum, b. p. 160°/3 mm., and set on cooling in tufts of cream needles, m. p. 70° (Found : Cl, 15·9. $C_{13}H_{11}OCl$ requires Cl, 16·3%). The acid chloride reacts with aniline to give 3 : 6-*dimethyl-2-naphthanilide*, pale straw-coloured, lustrous flakes from alcohol, m. p. 207—208° (Found : C, 82·9 ; H, 6·4. $C_{19}H_{17}ON$ requires C, 82·9 ; H, 6·2%).

Preparation and Pyrolysis of 2-p-Toluoyl-3 : 6-dimethylnaphthacene : 2 : 7-Dimethylnaphth-acene.—A small yield of the required ketone was obtained when 5·0 g. of 3 : 6-dimethyl-2-naphthoyl chloride, dissolved in dry toluene, were added, in portions, to 6·0 g. of sublimed ferric chloride covered with dry toluene, and the mixture heated at 90° for 4 hours. The product was decomposed with ice, and the toluene solution shaken with dilute caustic soda solution and water and evaporated to small bulk ; 2-*p*-*toluoyl*-3 : 6-*dimethylnaphthalene* (0·5 g.) then slowly crystallised. The ketone separated from petroleum (b. p. 60—80°) in large colourless plates, m. p. 112° (Found : C, 87·3 ; H, 6·75. $C_{20}H_{18}O$ requires C, 87·6 ; H, 6·6%). When heated

at 400°, it readily charred but formed a small amount of an orange sublimate. This was recrystallised from acetic acid and yielded golden-orange plates of 2 : 7-*dimethylnaphthacene*, m. p. 362° (Found :* C, 93·6; H, 6·5. $C_{20}H_{16}$ requires C, 93·7; H, 6·3%). The hydrocarbon closely resembles its 2 : 6-isomeride; it is sparingly soluble in the common solvents and its solutions show marked green fluorescence. In cold concentrated sulphuric acid it dissolves to a moss-green solution. When mixed with 2 : 6-dimethylnaphthacene, there is no marked depression of m. p.

2 : 7-*Dimethylnaphthacene*-9 : 10-*quinone*.—To the hydrocarbon (1·0 g.), suspended in 50 c.c. of boiling acetic acid, were added 1·2 g. of potassium dichromate in portions. The *quinone*, precipitated on dilution with water, crystallised from acetic acid, in which it was fairly readily soluble, in minute, short, flattened, yellow needles, m. p. 233° (Found : C, 83·8; H, 5·2. $C_{20}H_{14}O_{2}$ requires C, 83·9; H, 4·9%). The deep purple-red colour of the solution in concentrated sulphuric acid fades on dilution.

6-(2' : 4'-*Dimethyl*)*benzoyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (V).—Diphenylcarbamyl chloride (70 g.) was dissolved in tetralin (79 g.), an equal volume of carbon disulphide and powdered aluminium chloride (50 g.) were added, and the whole was heated under reflux for 3 hours. Carbon disulphide was then evaporated, and the residue poured on ice. The low-melting solid which separated, 1 : 2 : 3 : 4-*tetrahydro-6-naphthodiphenylamide*, crystallised from benzene-petroleum (b. p. 40—60°) in tufts of colourless, elongated, rhombic prisms, m. p. 87—88° (Found : C, 84·3; H, 6·7. $C_{23}H_{21}ON$ requires C, 84·4; H, 6·4%). The crude amide was boiled for ¼ hour with 140 c.c. of concentrated sulphuric acid and 84 c.c. of water and, after dilution and cooling, the precipitated solid was dissolved in ether and shaken with dilute caustic soda solution. Acidification of the soda extract gave 52·5 g. of crude 1 : 2 : 3 : 4-tetrahydro-6-naphthoic acid, which was crystallised from benzene, yielding 34·5 g., m. p. 154°. The acid chloride was obtained quantitatively by heating the acid under reflux for 4 hours with 3 times its weight of thionyl chloride and fractionally distilling the product in a vacuum (b. p. 163°/12 mm.). The acid and its chloride have been prepared by less convenient methods by v. Braun, Kirschbaum, and Schuhmann (*Ber.*, 1920, **53**, 1158, 1161). The acid chloride reacted with aniline to give 1 : 2 : 3 : 4-*tetrahydro-6-naphthanilide*, which crystallised from alcohol in colourless needles, m. p. 147° (Found : C, 80·9; H, 7·1. $C_{17}H_{17}ON$ requires C, 81·25; H, 6·8%).

1 : 2 : 3 : 4-Tetrahydro-6-naphthoyl chloride (28 g.) was dissolved in an equal volume of carbon disulphide and added gradually to powdered aluminium chloride (30 g.) covered with *m*-xylene (30 g.). After heating under reflux for 3 hours, the carbon disulphide was evaporated, and the reaction product decomposed with water. The viscid ketone which separated was washed with dilute sodium carbonate solution and water, dried and fractionally distilled in a vacuum. Yield, 36·5 g. of b. p. 223°/10 mm. Similarly, from 30 g. of 2 : 4-dimethylbenzoyl chloride, 30 g. of tetralin, and 30 g. of aluminium chloride, there were obtained 35·5 g. of the same viscid ketone. 6-(2' : 4'-*Dimethyl*)*benzoyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* is a pale yellow, viscid liquid which does not set even on long keeping (Found : C, 86·6, 86·0; H, 7·6, 7·8. $C_{19}H_{20}O$ requires C, 86·4; H, 7·6%).

Pyrolysis of 6-(2' : 4'-*Dimethyl*)*benzoyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* : 2-*Methylnaphthacene*.—When the ketone (50 g.) was boiled (bath temperature 400—420°), it darkened in colour and smoothly eliminated water. The product, cooled after 6 hours, partly crystallised. The crystals were separated, and the unchanged ketone repyrolysed. Finally about 30% conversion into a solid product, m. p. *ca.* 160°, was effected. The solid, fractionally crystallised from acetic acid, yielded 0·2 g. of 2-methylnaphthacene and a large fraction (15 g.) of a pale yellow, ill-defined, crystalline substance melting fairly sharply at 158° and consisting of 7-methyl-1 : 2 : 3 : 4-tetrahydronaphthacene (Calc. for $C_{19}H_{18}$: C, 92·7; H, 7·3%) and 7-methyl-1 : 2-benzanthracene (Calc. for $C_{19}H_{14}$: C, 94·2; H, 5·8%) (Found : C, 93·2, 93·5; H, 6·2, 6·2%). The mixture could not be separated by fractional crystallisation or by crystallisation of the mixed picrates and was dehydrogenated by heating with excess of selenium at 230° for 4 hours and then at 350° till nothing further sublimed. The sublimate (good yield) was fractionally crystallised from acetic acid and contained very pale yellow 7-methyl-1 : 2-benzanthracene, m. p. 181° (identified by oxidation to the corresponding quinone, m. p. 167°; Cook, J., 1932, 470), and 2-*methylnaphthacene*. The latter is a golden-orange hydrocarbon, m. p. 350°, similar in its properties to 2 : 6- and 2 : 7-dimethylnaphthacene but rather more soluble (Found : C, 93·2; H, 5·8. $C_{19}H_{14}$ requires C, 94·2; H, 5·8%). When oxidised with potassium dichromate in acetic acid, it gave a resinous substance (probably containing both 2-methylnaphthacene-9 : 10- and -11 : 12-quinones) which was not further examined.

Hydrogenation of 2 : 6- *and* 2 : 7-*Dimethylnaphthalenes*.—2 : 6-Dimethylnaphthalene was

first hydrogenated by C. C. Hall, who allowed full use to be made of his unpublished observations. The hydrocarbon (200 g.) was placed in a 2 l. autoclave with 100 atmospheres pressure of hydrogen and a catalyst made by impregnating 20 g. of active charcoal with a solution of 4 g. of molybdenum trioxide in ammonia solution, drying the mixture at 100°, and adding 4 g. of flowers of sulphur. The temperature was raised to 390—400° and maintained for 6 hours. On cooling, there was a residual pressure of 75 atmospheres; and the colourless liquid product, boiling between 180° and 244°, clearly contained more than one individual substance. Redistillation gave a fraction of b. p. 237—239° (25—30% of total product) which consisted of 2 : 6-*dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene* (Found : C, 90·3; H, 10·1. $C_{12}H_{16}$ requires C, 90·0; H, 10·0%). The limpid colourless oil set on cooling and melted at 14—17°. A smaller fraction, b. p. 215—220°, was washed repeatedly with concentrated sulphuric acid, and water, dried, and distilled; it then boiled at 216—217° and had the composition of 2 : 6-*dimethyldecalin*. It was an oil which did not set when cooled to 0° and had a characteristic terpene-like odour (Found : C, 86·7; H, 13·4. $C_{12}H_{22}$ requires C, 86·8; H, 13·2%). Six racemic forms of stereo-isomeric 2 : 6-dimethyldecalins are possible (3 derived from *cis*-decalin and 3 from the *trans*-isomeride) and if this fraction is a pure specimen of one of these it is probable that others are formed in the hydrogenation and are contained in the other fractions of b. p. below 237°. The latter were sulphonated together and gave a quantity of pure sodium 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-7-sulphonate when the crude salt was recrystallised from water.

When the hydrogenation was carried out at a lower temperature and for a shorter time, the product contained much unchanged 2 : 6-dimethylnaphthalene.

2 : 7-Dimethylnaphthalene (250 g.) was hydrogenated for 4 hours at 300° with an initial pressure of 100 atmospheres of hydrogen and the same proportion of the same catalyst. The crude water-white liquid hydrogenation product yielded, on fractional distillation, 70 g. of unchanged hydrocarbon; a liquid, boiling over the range 180—237°, which did not appear to contain a preponderant individual substance, but yielded an appreciable proportion of pure sodium 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-6-sulphonate; and 84 g. of 2 : 7-*dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene*, b. p. 237—238°, m. p. below 0° (Found : C, 90·0; H, 10·1%). When the hydrogenation was effected at 390—400°, the product contained very little unchanged 2 : 7-dimethylnaphthalene and a smaller proportion of the tetralin, but an oil, of b. p. 216—218°, inert to concentrated sulphuric acid in the cold and of a fragrant terpene-like odour was separated by fractional distillation (Found : C, 86·6; H, 13·3%). If this is one of the 6 isomerides of 2 : 7-*dimethyldecalin*, others are probably contained in the rest of the hydrogenation product which boils between 180° and 235°.

2 : 6-*Dimethyl-1 : 2 : 3 : 4-tetrahydro-7-naphthoic Acid.*—Powdered aluminium chloride (25 g.) was added to a mixture of diphenylcarbamyl chloride (35 g.), 2 : 6-dimethyltetralin (20 g.), and carbon disulphide (30 c.c.), and the whole warmed gently for 6 hours. Carbon disulphide was then evaporated, and the residue poured on ice. The crude viscid 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydro-7-naphthodiphenylamide which separated was boiled during ¼ hour with 170 g. of 75% sulphuric acid and the mixture of crude acid and diphenylamine, which crystallised on cooling and dilution, was treated with cold dilute sodium carbonate solution. 2 : 6-*Dimethyl-1 : 2 : 3 : 4-tetrahydro-7-naphthoic acid* (4·0 g.), precipitated from the soda solution, crystallised from aqueous acetic acid in colourless elongated prisms or needles, m. p. 183° (Found : C, 76·5; H, 8·1. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%). When heated with thrice its weight of selenium for 4 hours at 250—300°, it lost hydrogen, and the product, recrystallised from acetic acid, yielded 2 : 6-dimethyl-3-naphthoic acid, identified by comparison with an authentic specimen.

2 : 7-*Dimethyl-1 : 2 : 3 : 4-tetrahydro-6-naphthoic Acid.*—From 2 : 7-dimethyltetralin (22 g.) there was obtained, by similar methods to those described above, a poor yield (4·0 g.) of 2 : 7-*dimethyl-1 : 2 : 3 : 4-tetrahydro-6-naphthoic acid*, colourless needles or prisms, m. p. 187° (Found : C, 76·5; H, 8·1%). On dehydrogenation (see 2 : 6-isomeride above) it yielded 3 : 6-dimethyl-2-naphthoic acid.

2 : 6-*Dimethyl-1 : 2 : 3 : 4-tetrahydro-7-naphthol.*—When shaken at 40° with concentrated sulphuric acid (40 g.), 2 : 6-dimethyltetralin (20 g.) dissolved rapidly to a deep red solution. The crude sulphonic acid was precipitated on addition of water, but dissolved on further dilution. The barium salt was crystallised from water, in which it was slightly soluble, and converted into the sparingly soluble sodium sulphonate (25 g.). This was powdered, and heated on the steam-bath with an equal weight of phosphorus pentachloride for 1 hour, and the product treated with cold water to precipitate the viscid sulphonyl chloride, which was boiled with ammonia solution (*d* 0·880) for 3 hours. An almost theoretical yield (from the sodium sulphonate) of 2 : 6-*dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-7-sulphonamide*, cream needles, m. p.

166—167°, from alcohol–water, resulted (Found : S, 13·3. $C_{13}H_{17}O_8NS$ requires S, 13·4%). The sodium salt (15 g.) was fused for ¼ hour at 300—340° with 60 g. of caustic potash and a few c.c. of water, and the product diluted and acidified. The dark brown, viscid precipitate was dissolved in ether, shaken with sodium bicarbonate solution and water, ether evaporated, and the residue distilled. The fraction, b. p. 280—300°, set on cooling and was crystallised from benzene–petroleum (b. p. 40—60°), 5 g. of 2 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro-7-naphthol*, colourless needles of phenolic odour, m. p. 116°, being obtained (Found : C, 81·9 ; H, 9·0. $C_{12}H_{16}O$ requires C, 81·8 ; H, 9·1%). When it was mixed with four times its weight of a sample of phenols of low " wetting power," the " wetting time " fell from 240 to 26 seconds (see Morgan, Pratt, and Pettet, *J. Soc. Dyers and Colourists*, 1933, 49, 125). The tetrahydronaphthol was dehydrogenated by heating at 240° for 4 hours with selenium and gave 2 : 6-dimethyl-3-naphthol, identical with an authentic specimen.

2 : 7-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydro-6-naphthol*.—2 : 7-Dimethyltetralin (20 g.) was sulphonated as readily as the 2 : 6-isomeride when shaken with concentrated sulphuric acid (40 g.). The product was diluted to 300 c.c., neutralised with caustic soda, boiled, and cooled, whereupon 25 g. of the sodium sulphonate crystallised in pearly flakes. 2 : 7-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydro-6-sulphonamide*, cream needles, m. p. 145·5°, from aqueous alcohol, was obtained almost quantitatively through the sulphonyl chloride (see preparation of 2 : 6-isomeride, above) (Found : S, 13·4%). The sodium sulphonate (22 g.) was fused with caustic potash (90 g.) (see preparation of 2 : 6-isomeride, above) and gave 5 g. of a crude product, b. p. 260—300°, m. p. 90—130°, from which was isolated, by fractional distillation and crystallisation, 2 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro-6-naphthol*, colourless needles with phenolic odour, m. p. 87°, from benzene–petroleum (b. p. 40—60°) (Found : C, 81·95 ; H, 9·0. $C_{12}H_{16}O$ requires C, 81·8 ; H, 9·1%). The less volatile portion of the crude product was recrystallised from benzene–petroleum (b. p. 40—60°) and furnished flaky crystals of 3 : 6-dimethyl-2-naphthol, m. p. 172° (compared with an authentic specimen).

Condensation of 2 : 6- and 2 : 7-Dimethyltetralin with p-Toluoyl and Benzoyl Chlorides.—The dimethyltetralin was dissolved in an equal volume of carbon disulphide, the theoretical amount of acyl chloride added, and then an equal weight of powdered aluminium chloride in portions. After boiling during ¼ hour, the reaction product was poured on ice, the viscid ketone taken up in ether and shaken with dilute caustic soda solution and water, and, after removal of ether, the residual crude ketone purified by fractional distillation or crystallisation. In each case the yield was almost quantitative. 7-p-*Toluoyl*-2 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* formed large colourless rhombs, m. p. 95°, from benzene–petroleum (b. p. 40—60°) (Found : C, 86·4 ; H, 8·1. $C_{20}H_{22}O$ requires C, 86·3 ; H, 7·9%).

6-*Benzoyl*-2 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* is a colourless viscid liquid, b. p. 202°/4 mm., 199°/3 mm. (Found : C, 86·1 ; H, 7·9. $C_{19}H_{20}O$ requires C, 86·4 ; H, 7·6%). 6-p-*Toluoyl*-2 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, a colourless viscid liquid, b. p. 199°/2 mm., crystallised when cooled to −80°, but melted on warming to room temperature (Found : C, 86·3 ; H, 8·1%).

Pyrolysis of Ketones.—When gently boiled under reflux, 7-*p*-toluoyl-2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene smoothly lost water, and to a less extent hydrogen. The pyrolytic product (yield, about 30%) was removed at intervals, and the recovered ketone repyrolysed. The solid product was fractionally crystallised from acetic acid and furnished a small quantity of the sparingly soluble 2 : 6-dimethylnaphthacene, m. p. 365°, but the rest consisted of 2 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthacene*, pale yellow, anthracene-like flakes, m. p. 214° (Found : C, 92·4 ; H, 7·7. $C_{20}H_{20}$ requires C, 92·3 ; H, 7·7%). 6-Benzoyl-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene similarly yielded on pyrolysis 2-methylnaphthacene and 2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthacene*, pale yellow flakes, m. p. 203° (Found : C, 92·7 ; H, 7·6. $C_{19}H_{18}$ requires C, 92·7 ; H, 7·3%). 6-Toluoyl-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene gave mainly 2 : 7-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthacene*, pale yellow flakes from acetic acid, m. p. 210° (Found : C, 92·1 ; H, 7·5. $C_{20}H_{20}$ requires C, 92·3 ; H, 7·7%) ; but again a small amount of the dehydrogenated 2 : 7-dimethylnaphthacene was present in the crude product. The tetrahydro-derivatives are much more soluble than the naphthacene homologues and are easily separated from them.

Dehydrogenation of Tetrahydronaphthacene Derivatives.—2-Methyl-, 2 : 6- and 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthacenes were all dehydrogenated smoothly by heating with selenium at 240° for 4 hours. The temperature was raised to 300—350° and the corresponding naphthacene homologue, which sublimed, was recrystallised from acetic acid.

Oxidation of 2 : 6- and 2 : 7-Dimethyl-1 : 2 : 3 : 4-*tetrahydronaphthacenes.*—When the tetra-

hydro-derivatives (1 g.) were oxidised, by addition of potassium dichromate to a boiling acetic acid solution, mixed quinone-like products were obtained unless at least 2 g. of dichromate were used.   From 2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthacene there was then obtained a good yield of pure 2 : 7-dimethylnaphthacene-9 : 10-quinone, identified by analysis (Found : C, 83·6; H, 5·3%) and comparison by mixed m. p. with an authentic specimen.   From the other isomeride there was similarly obtained 2 : 6-dimethylnaphthacene-9 : 10-quinone.

17.   *The Catalytic Hydrogenation of Diphenyl Triketone.   Part I.*

By LUCIUS A. BIGELOW, H. GORDON RULE, and W. A. P. BLACK.

THE catalytic hydrogenation of benzil and its derivatives has been shown to be a simple and effective method of obtaining the numerous reduction products of these 1 : 2-diketones (Buck and Jenkins, *J. Amer. Chem. Soc.*, 1929, **51**, 2163; Buck, Jenkins, and Bigelow, *ibid.*, 1930, **52**, 4495, 5198).   It seemed, therefore, that the method might well be applied with success to the more complex case of a 1 : 2 : 3-triketone, and this paper describes the first steps in the catalytic reduction of the simplest possible aromatic triketone, $C_6H_5 \cdot CO \cdot CO \cdot CO \cdot C_6H_5$.   The theoretical possibilities are relatively numerous owing to isomerisation, but the first changes may be summarised in the following scheme :

$$\text{Ph·CO·CO·COPh} \xrightarrow{\text{2H}} \text{Ph·CO·CH(OH)·COPh} \quad \text{(I.)}$$

$$\text{Ph·CH(OH)·CH(OH)·CH(OH)Ph} \quad \text{(III.)}$$

$$\text{Ph·CH(OH)·CO·CH(OH)Ph} \rightleftarrows \text{Ph·CH(OH)·CH(OH)·COPh} \quad \text{(II.)}$$
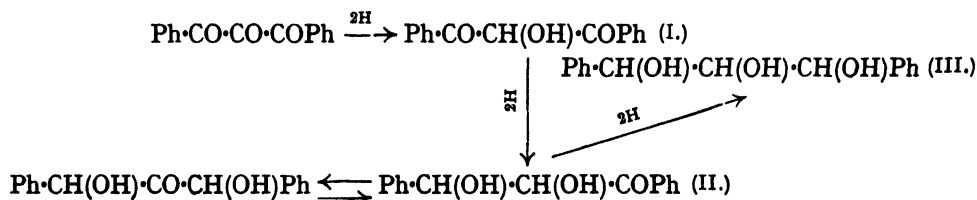
The reactions were carried out at room temperature in the well-known Adams apparatus as described by Buck and Jenkins (*loc. cit.*), the usual platinum–platinum oxide catalyst being used.   Pure benzene was employed as solvent and the reduction occurred readily under a pressure of 2—5 atmospheres.   The character and quantity of the catalyst, however, had a marked influence upon the speed of reaction and, by adjusting the amount used, the triketone could be made to take up 1, 2, or 3 moles of hydrogen at will.

When allowed to take up 1 mole of hydrogen, the triketone yielded *dibenzoylcarbinol* (I).   On treatment with acetyl chloride the carbinol was converted into the acetyl derivative described by Neufville and Pechmann (*Ber.*, 1890, **23**, 3375).

Dibenzoylcarbinol readily underwent further hydrogenation.   Rapid reduction led without any break in the time–pressure curve to the absorption of 2 moles of hydrogen, with formation of αγ-*diphenylglycerol* (III).   On employing a smaller amount of catalyst, a break in the hydrogenation became evident after the absorption of 1 mole, at which point crystals of diphenylglycerol began to separate.   A point of interest lies in the structural resemblance between this compound and trihydroxyglutaric acid, which exists in two *meso*- and two optically active forms.   It is hoped to deal more fully with this problem in a later communication.

In the hydrogenation of either dibenzoylcarbinol or diphenyl triketone with a suitable amount of catalyst, a break in the time–pressure curve was noted at the stage corresponding to the formation of the intermediate *dihydroxy*-compound (II).   When the absorption was interrupted at this point, an oil was obtained, purifiable with some loss to give colourless

needles which exhibited small variations in melting point according to the rate of heating. This compound readily underwent further hydrogenation to form diphenylglycerol in good yield, but acetylation gave rise only to an uncrystallisable oil. The variable melting point and difficulty of isolating any definite acetyl derivative suggest that the dihydroxy-compound readily isomerises on heating or in solution.

<div align="center">EXPERIMENTAL.</div>

The platinum catalyst was prepared by the method of Adams ("Organic Syntheses," 1928, **8**, 92), and the diphenyl triketone, m. p. 69—70°, by the method of Bigelow and Hauslick (*op. cit.*, 1933, **13**, 38). A preliminary calibration of the apparatus was carried out for the absorption of one and two molecular proportions of hydrogen, using 0·01 mole of pure benzoin and benzil respectively as standards. Complete hydrogenation to hydrobenzoin corresponded in the first case to a fall of 16 lb./sq. in. in pressure and in the second case to 32 lb./sq. in. All hydrogenations were carried out under pressures of 2—3 atmospheres, except in the direct reduction of the triketone to diphenylglycerol, where an initial pressure of 5 atmospheres was employed.

Dibenzoylcarbinol from Diphenyl Triketone.—A solution of 2·38 g. (0·01 mole) of diphenyl triketone in 50 c.c. of pure benzene containing 0·05 g. of the catalyst in suspension was hydrogenated at 15° until after 1 hour the pressure had fallen 16 lb., corresponding to the absorption of 0·01 mole of hydrogen. The catalyst was then removed, and the volume of the filtrate reduced to 20 c.c. by evaporation under diminished pressure at room temperature. Colourless needles separated (1·45 g.), m. p. 100—104°. Recrystallisation from 150 c.c. of ligroin (b. p. 80—100°) gave 1·15 g. of long needles, which melted at 110—111·5° to a yellow liquid, the m. p. being unaffected by further crystallisation from alcohol (Found : C, 75·0; H, 5·1; *M*, by the Menzies–Wright method, 238. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%; *M*, 240). The colourless solid turns yellow at 100°, and if maintained at 106—107° it melts, resolidifies, and again melts to a deep yellow liquid, the complete series of changes occupying about 15 minutes. The final equilibrium mixture (of isomerides ?) thus obtained solidifies on cooling and then melts at 96—98°.

Dibenzoylcarbinol dissolves readily in alcohol and ether, moderately readily in benzene, and more sparingly in ligroin, develops a light orange coloration when shaken in benzene solution with sulphuric acid (the triketone develops a blue colour), and gives no coloration with alcoholic ferric chloride.

The carbinol (1 g.), on treatment with 20 c.c. of acetyl chloride at 50° for ½ hour, gave the acetyl derivative (92% yield), separating from methyl alcohol in rhombic plates, m. p. 93° alone or admixed with an authentic specimen prepared by the method of Neufville and Pechmann (*loc. cit.*).

αγ-Diphenylglycerol from Dibenzoylcarbinol.—The carbinol (2·40 g., 0·01 mole) in 50 c.c. of benzene was reduced at room temperature by 0·10 g. of catalyst, until after 1 hour 2 mols. of hydrogen had been absorbed. No further hydrogenation could be effected by aeration of the catalyst or by addition of fresh catalyst. The syrup obtained by filtering the hot solution from the catalyst and evaporating the solvent crystallised when covered with light petroleum; m. p. 80—82° (yield, 97% of the theoretical). The crude product dissolved readily in hot benzene (45 c.c.) to a highly refracting solution, which deposited colourless needles or prisms. After being dried for several hours at 60°, or maintained in a vacuum over calcium chloride for several days, these gave the anhydrous compound, m. p. 84·5—85° [Found : C, 73·8; H, 6·5; *M*, in boiling benzene (*c* = 0·4, 0·64), 244, 246. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·5%; *M*, 244]. When the finely divided compound was kept over-night in a moist atmosphere, it was converted quantitatively into the *monohydrate*, m. p. 97—99°, also obtainable in rhombic plates by crystallising the anhydrous form from aqueous (1 : 1) alcohol (Found : C, 68·8; H, 6·9. $C_{15}H_{16}O_3,H_2O$ requires C, 68·7; H, 6·9%). *Diphenylglycerol* exhibits a very strong tendency to undergo hydration. If the anhydrous compound is crystallised from a small amount of dry benzene without filtration, the solution deposits the pure anhydrous product. When small quantities of such a solution are filtered through filter-paper which has not been specially dried, the deposited crystals are of the hydrated form. In a desiccator over calcium chloride, complete dehydration requires about a fortnight, the m. p. of the product passing through a minimum value of 80—81°.

Diphenylglycerol has a sweet taste and is appreciably soluble in water. It dissolves readily in alcohol and ether, is moderately soluble in benzene and sparingly in light petroleum. A

benzene solution shaken with concentrated sulphuric acid gives a characteristic bright red coloration. The solid compound dissolves in sulphuric acid to a brilliant purple solution.

Diphenylglycerol (1 g.) was boiled for 30 minutes with 20 c.c. of acetic anhydride. When the cooled solution was poured into water, 1·4 g. (93% yield) of the *triacetate* were deposited, m. p. 84—85°. The pure derivative separated from alcohol in plates, m. p. 85—86° (Found : C, 68·1; H, 5·8; CH_3·CO, 34·0. $C_{21}H_{22}O_6$ requires C, 68·1; H, 6·0; CH_3·CO, 35·0%). On admixture with diphenylglycerol the product melted at 67—70°. The triacetate on hydrolysis regenerated diphenylglycerol.

When the above hydrogenation was repeated with a smaller amount of catalyst (0·075 g.), a deposition of crystalline diphenylglycerol began as soon as 1 mol. of hydrogen had been absorbed. This deposit appeared to envelop and deactivate the catalyst, with the result that the absorption of the final molecular proportion of hydrogen occupied 3 hours.

Diphenyl triketone (2·38 g.) in 50 c.c. of benzene was converted into diphenylglycerol in one operation by using 0·15 g. of the catalyst and an initial pressure of 5 atmospheres. The first molecular proportion of hydrogen was absorbed in 30 minutes, and the second in 40 minutes. The third stage occupied 4 hours, apparently owing to the crystalline deposit carrying down part of the catalyst. An almost theoretical yield was obtained.

All the hydrogenations described in this paper may be carried out in glacial acetic acid or 95% alcohol as solvent : in the majority of cases the reaction is completed more rapidly than in benzene. For example, diphenyl triketone in alcohol was converted into diphenylglycerol (87% yield) in 2 hours, as compared with 4 or 5 hours for a benzene solution. The latter solvent is, however, more suitable for the final purification.

αβ-*Dihydroxy-γ-keto-αγ-diphenylpropane or an Isomeride thereof.*—Dibenzoylcarbinol (2·40 g.) was reduced as above, 0·05 g. of catalyst being used, until after 2 hours 0·01 mole of hydrogen had been absorbed. After filtration the pale yellow solution was seeded with diphenylglycerol and kept over-night; 0·3 g. of diphenylglycerol (hydrated form) was then deposited and removed. Evaporation of the solvent left a white solid (1·9 g.), m. p. 67—70°, which on being twice recrystallised from ligroin (b. p. 100—120°) gave colourless well-formed needles (0·6 g.), m. p. 87—89°. As in the case of dibenzoylcarbinol, fusion is accompanied by a colour change to yellow (Found : C, 74·2; H, 5·9. $C_{16}H_{14}O_3$ requires C, 74·4; H, 5·8%). The same product, m. p. 86—88°, was obtained by reducing 2·38 g. of diphenyl triketone, using 0·1 g. of catalyst and 50 c.c. of benzene, until 2 mols. of hydrogen had been absorbed.

The *dihydroxy*-compound strongly depresses the melting points of dibenzoylcarbinol and of diphenylglycerol It dissolves in sulphuric acid to a clear yellow solution, which gradually turns red and develops a green fluorescence. An alcoholic solution gives no coloration with ferric chloride. The solubility in organic solvents is intermediate between that of the related carbinol and glycerol.

Hydrogenation of the dihydroxy-compound (1·21 g.) in benzene (30 c.c.) with 0·05 g. of catalyst converted it in 40 minutes into diphenylglycerol (1·0 g.). The latter was deposited from benzene in rhombic plates of the hydrated form, m. p. 97—98°.

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18. *Reactions of* o-*Hydroxybenzylidenediacetophenones. Part II. Conversion into Pyrylium and Benzopyrylium Salts.*

By DOUGLAS W. HILL.

DILTHEY and his collaborators have shown that benzylidenediacetophenones are converted into triphenylpyrylium salts by the action of ferric chloride in acetic anhydride (*J. pr. Chem.,* 1916, **94**, 53; 1917, **95**, 107; *Ber.,* 1917, **50**, 1008; 1919, **52**, 1195; 1920, **53**, 252). It is at once apparent that such a reaction applied to the *o*-hydroxy-derivatives might lead either, by ring closure of the enolic form of the ketonic side chains, to 2 : 6-diphenyl-4-(*o*-hydroxyphenyl)pyrylium salts of type (I) or, by ring closure on the phenolic hydroxyl, to 4-phenacylflavylium salts of type (III). A representative of the latter class of compound

was described by Irvine and Robinson (J., 1927, 2086), who prepared 6-methoxy-4-phenacylflavylium ferrichloride by the action of hydrogen chloride on 6-methoxy-4-phenacylideneflavene, followed by the addition of ferric chloride. Dilthey and Floret (*Annalen,* 1924, **440**, 89) obtained salts of type (I)—with an *o*-hydroxyl group in the 4-phenyl nucleus—by demethylation of the salts formed from *o*-methoxybenzylidenediacetophenone.

The preparation of triphenylpyrylium salts as described by Dilthey has been confirmed by experiments on benzylidenediacetophenone, *o*-methoxy-, *p*-methoxy-, and 2 : 4-dimethoxy-benzylidenediacetophenones, all of which yielded the corresponding triphenylpyrylium salts when treated in acetic anhydride with a solution of ferric chloride in 20% hydrochloric acid. On passing to the *o*-hydroxy-derivatives, however, the results were different. The previous reactions had always been vigorous, but when carried out in the same way with *o*-hydroxybenzylidenediacetophenones, only simple flavylium salts of type (II) could be isolated : the phenacyl group in position 4 had been eliminated. Triphenylpyrylium salts of type (I) in which both salt formation and acetylation of the hydroxy-group had occurred were obtained by maintaining the temperature during the reaction at about 25°.

The 4-phenacylflavylium salts which might reasonably have been expected in the first case from the above reaction were readily prepared by the method of Irvine and Robinson (*loc. cit.*) starting from the 4-phenacylideneflavenes. The same salts might also be expected to be formed by this method from the parent *o*-hydroxybenzylidenediacetophenones or from the 4-phenacylflavenes intermediate between the diacetophenones and the phenacylideneflavenes (see Part I, J., 1934, 1255). Contrary to expectation, in both cases the products were, not 4-phenacylflavylium salts, but simple flavylium salts unsubstituted in position 4. The indications previously obtained of the ease with which the phenacyl-group is removed from these compounds are emphasised by these results and it appears that the formation of flavylium salts from them is dependent on the elimination of the 4-substituent, except in the case of 4-phenacylideneflavenes where unsaturation, to which the salt-forming groups can add, occurs at the 4-position. Dilthey has shown that, in the benzopyrylium salts he has examined, salt formation occurs on the 2-carbon atom (*J. pr. Chem.,* 1933, **188**, 42). The results now obtained indicate that in other cases the 4-carbon may be the heteropolar atom.

The reaction scheme given in Part I can now be extended as shown below, in which Dilthey's " carbenium " formula has been adopted for the salts.
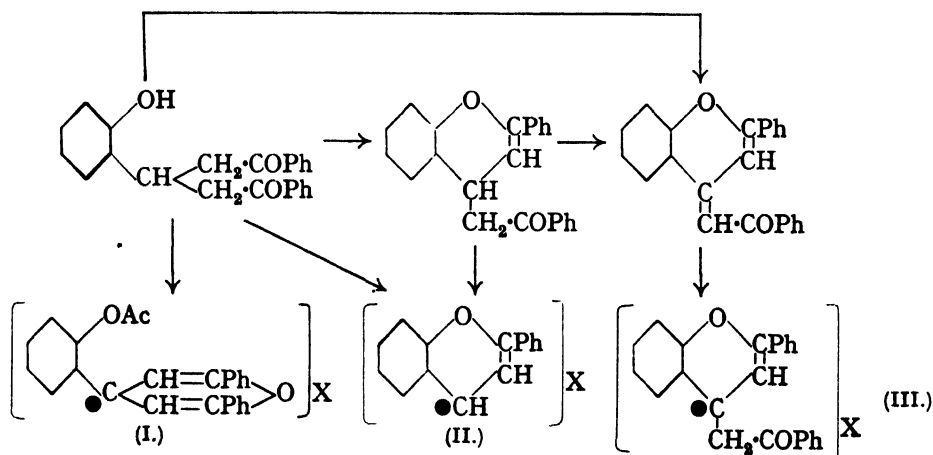
Flavylium Ferrichloride.—(a) Through a suspension of *o*-hydroxybenzylidenediacetophenone (5 g.) in glacial acetic acid (30 c.c.), dry hydrogen chloride was rapidly passed for 5 minutes, with cooling. Ferric chloride (2·5 g., anhydrous) in acetic acid (15 c.c.), added to the deep red solution, at once produced a brown crystalline ferrichloride. Collected after an hour

and recrystallised from glacial acetic acid, this formed golden-yellow plates, m. p. 140° (flavylium ferrichloride prepared from chalkone melts at 140°) (Found : C, 44·45; H, 2·9; Fe, 13·5; Cl, 34·9. Calc. for $C_{15}H_{11}OCl_4Fe$: C, 44·4; H, 2·7; Fe, 13·5; Cl, 35·05%).

(b) A similar procedure with 4-phenacylflavene (2 g.) in glacial acetic acid (10 c.c.) gave an orange-yellow ferrichloride, which crystallised from glacial acetic acid in golden-yellow plates, m. p. 138°.

(c) A suspension of o-hydroxybenzylidenediacetophenone (1 g.) in acetic anhydride (10 c.c.) was treated, with stirring but without cooling, with ferric chloride (1 g.) in 20% hydrochloric acid (5 c.c.); a vigorous reaction occurred. The precipitate was collected after 12 hours; it crystallised from glacial acetic acid in golden-yellow blades, m. p. 138° (Found : C, 44·7; H, 2·8; Fe, 13·5%).

Flavylium Perchlorate.—Dry hydrogen chloride was passed through a suspension of o-hydroxybenzylidenediacetophenone (2 g.) in a mixture of dry ether (25 c.c.) and 20% perchloric acid (10 c.c.) for 4 hours; after 12 hours, the deep red solution was treated with dry ether. The precipitated perchlorate crystallised from glacial acetic acid in golden-yellow plates, m. p. 184° alone or mixed with an authentic specimen (Löwenbein, *Ber.*, 1924, **57**, 1526, describes yellow plates with a metallic sheen, m. p. 186—187°).

6-Methoxyflavylium Ferrichloride.—(a) 2-Hydroxy-5-methoxybenzylidenediacetophenone (2 g.) was suspended in glacial acetic acid and treated as described in (a) above. The ferrichloride separated from glacial acetic acid as brown platelets with a greenish-golden sheen, m. p. 205° (Irvine and Robinson describe the salt as brown platelets with green nuance, m. p. 203°).

(b) The same procedure with 6-methoxy-4-phenacylflavene (1·5 g.) led to a solid ferrichloride, which separated from glacial acetic acid as brown platelets with a green sheen, m. p. 204—205°.

7-Methoxyflavylium Ferrichloride.—(a) 2-Hydroxy-4-methoxybenzylidenediacetophenone (1 g.), suspended in dry ether (50 c.c.), was treated with a rapid stream of dry hydrogen chloride. The yellow flocculent precipitate was collected after 12 hours, washed with dry ether, and dissolved in warm concentrated hydrochloric acid. An excess of ferric chloride dissolved in concentrated hydrochloric acid was added and the precipitated oil was allowed to solidify and then crystallised twice from glacial acetic acid, forming brown needles, m. p. 147° (Found : C, 44·3; H, 3·1; Fe, 12·3; Cl, 32·0. Calc. for $C_{16}H_{13}O_2Cl_4Fe$: C, 44·1; H, 3·0; Fe, 12·9; Cl, 32·6%).

(b) A suspension of 2-hydroxy-4-methoxybenzylidenediacetophenone (3 g.) in acetic anhydride (20 c.c.) was treated, with stirring but without cooling, with ferric chloride (1·5 g.) in 20% hydrochloric acid (7 c.c.). The solid that separated slowly on cooling crystallised from acetone, on addition of ether, as brown needles, m. p. and mixed m. p. 147°.

7-Methoxyflavylium perchlorate, prepared, in the manner previously described for flavylium perchlorate, from the diketone (1 g.) in dry ether (50 c.c.) and 20% perchloric acid (10 c.c.), crystallised from glacial acetic acid in bright yellow needles, m. p. and mixed m. p. 222°.

4-Phenacylflavylium Ferrichloride.—A rapid stream of dry hydrogen chloride was passed through 4-phenacylideneflavene (2 g.) in glacial acetic acid (10 c.c.) for 10 minutes. The deep red solution was then treated with ferric chloride (1 g. in 10 c.c. of glacial acetic acid). The oily precipitate formed solidified when scratched; it was washed with ether and crystallised from glacial acetic acid, separating as orange-coloured needles, m. p. 156—157° (Found : C, 52·45; H, 3·2; Fe, 10·7; Cl, 27·2. $C_{23}H_{17}O_2Cl_4Fe$ requires C, 52·3; H, 3·25; Fe, 10·7; Cl, 27·15%).

6-Methoxy-4-phenacylflavylium ferrichloride, prepared as described by Irvine and Robinson (*loc. cit.*), crystallised from glacial acetic acid in red-brown needles, m. p. 173—174° (decomp.) (Irvine and Robinson give m. p. 170° with blackening).

7-Methoxy-4-phenacylflavylium Ferrichloride.—The usual procedure (suspension of 7-methoxy-4-phenacylideneflavene, 2 g., in cold glacial acetic acid, 20 c.c.; rapid stream of dry hydrogen chloride for 3 minutes; ferric chloride, 1 g., in 10 c.c. of glacial acetic acid) gave a precipitate which, recrystallised from glacial acetic acid, formed fine, matted, yellow needles, m. p. 168° (Found : C, 51·95; H, 3·5; Fe, 10·4; Cl, 25·6. $C_{24}H_{19}O_3Cl_4Fe$ requires C, 52·1; H, 3·4; Fe, 10·1; Cl, 26·3%).

2 : 6-Diphenyl-4-(2′ : 4′-dimethoxyphenyl)pyrylium Ferrichloride.—A solution of 2 : 4-dimethoxybenzylidenediacetophenone (3 g.) in acetic anhydride (20 c.c.) was stirred and treated, without cooling, with a solution of anhydrous ferric chloride (1·5 g.) in 20% hydrochloric acid (7 c.c.), added drop by drop; a vigorous reaction occurred. The red oil obtained solidified on cooling; collected after 12 hours, the solid crystallised from cold acetone, on addition of ether, in red needles, m. p. 190—191° (Found : C, 53·1; H, 4·0; Fe, 9·5; Cl, 24·1. $C_{25}H_{21}O_3Cl_4Fe$ requires C, 52·9; H, 3·7; Fe, 9·9; Cl, 25·0%).

2 : 6-*Diphenyl*-4-(o-*acetoxyphenyl*)*pyrylium Ferrichloride.*—To a stirred and well-cooled suspension of o-hydroxybenzylidenediacetophenone (5 g.) in acetic anhydride (40 c.c.), a solution of ferric chloride (5 g.) in 20% hydrochloric acid (20 c.c.) was added very slowly, rise of temperature being prevented. Stirring was continued for an hour and the precipitate was collected and crystallised several times from glacial acetic acid, forming greenish-brown plates, m. p. 181° (Found : C, 53·1; H, 3·4; Fe, 9·8; Cl, 24·8. $C_{25}H_{19}O_2Cl_4Fe$ requires C, 53·1; H, 3·4; Fe, 9·9; Cl, 25·1%).

2 : 6-*Diphenyl*-4-(2'-*acetoxy*-4'-*methoxyphenyl*)*pyrylium Ferrichloride.*—2-Hydroxy-4-methoxybenzylidenediacetophenone (2 g.) was suspended in acetic anhydride (35 c.c.) and treated below 25° with ferric chloride (1·5 g.) in 20% hydrochloric acid (7 c.c.). A small amount of solid separated, and more on addition of dry ether. It crystallised from glacial acetic acid in purple-brown needles, m. p. 162° (Found : C, 52·35; H, 3·5; Fe, 9·2; Cl, 24·0. $C_{26}H_{21}O_4Cl_4Fe$ requires C, 52·4; H, 3·5; Fe, 9·4; Cl, 23·9%).

2 : 6-*Diphenyl*-4-(2'-*acetoxy*-5'-*methoxyphenyl*)*pyrylium Ferrichloride.*—The reaction described above was carried out with 2-hydroxy-5-methoxybenzylidenediacetophenone (3 g.) in acetic anhydride (20 c.c.). The solid obtained, crystallised from cold acetone by the addition of ether, formed long, slender, golden-yellow needles with a greenish lustre, m. p. 225—226° (Found : C, 52·4; H, 3·6; Fe, 9·3; Cl, 23·85. $C_{26}H_{21}O_4Cl_4Fe$ requires C, 52·4; H, 3·5; Fe, 9·4; Cl, 23·9%).

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19. *Reactions of* o-*Hydroxybenzylidenediacetophenones. Part III. Formation of a 4-Phenacylideneflavene during the Preparation of 4'-Methoxyflavylium Chloride.*

By DOUGLAS W. HILL and R. R. MELHUISH.

SINCE benzylidenediacetophenones without an o-hydroxyl group are readily prepared by the agency of hydrogen chloride (Blumstein and Kostanecki, *Ber.*, 1900, **33**, 1481; Rupe and Veit, *Chem. Zentr.*, 1906, I, 1417), it is apparent that the condensation of o-hydroxybenzaldehydes and acetophenones to give flavylium salts may result in the formation of appreciable amounts of the corresponding o-hydroxybenzylidenediacetophenones. Besides diminishing the yield of the desired product, these compounds are capable of forming 4-phenacylflavylium salts which may contaminate the final material. In glacial acetic acid, these o-hydroxybenzylidenediacetophenones are converted smoothly and rapidly into the simple flavylium salts (preceding paper) and the question of contamination appears therefore to be eliminated. The condensation of aldehyde and acetophenone is, however, often carried out in ether and we have repeatedly found that attempts to prepare flavylium ferrichloride by treatment of o-hydroxybenzylidenediacetophenone with hydrogen chloride in ethereal solution resulted in a well-defined crystalline salt, giving analyses in which the values for carbon and hydrogen were high and for iron and chlorine low. Repeated crystallisations of the salt from glacial acetic acid failed to improve these values and we were forced to conclude that the salt was contaminated by the presence of 4-phenacylflavylium ferrichloride.

We have demonstrated the production of a 4-phenacylflavylium salt in at least one such case. When salicylaldehyde and *p*-methoxyacetophenone are condensed by means of hydrogen chloride in dry ether and the resulting flavylium chloride is taken up in 0·5% hydrochloric acid, a part of the product is decomposed with the formation of 4'-*methoxy*-4-(p-*methoxyphenacylidene*)*flavene.* The same compound is obtained in the usual manner from o-*hydroxybenzylidenedi*-(p-*methoxyacetophenone*), which behaves normally with acids and can be converted also into 4'-*methoxy*-4-(p-*methoxyphenacyl*)*flavene.* The phenacylidene

derivative yields 4'-methoxy-4-(*p*-methoxyphenacyl)flavylium salts, of which the *chloride* is immediately hydrolysed in 0·5% hydrochloric acid to 4'-methoxy-4-(*p*-methoxyphen-acylidene)flavene. There can therefore be no doubt that this salt is formed together with the simple flavylium chloride during the condensation referred to above, and the possibility of the formation of such salts as by-products of the preparation of flavylium salts in ether by this procedure cannot be overlooked.

<div align="center">EXPERIMENTAL.</div>

Action of Hydrogen Chloride on o-*Hydroxybenzylidenediacetophenone in Ether.*—The diaceto-phenone (3 g.) was suspended in dry ether, and dry hydrogen chloride rapidly passed through it for 2 hours. After 12 hours, the chloride separated as thick red needles. The salt was unstable and the reaction mixture was therefore extracted with concentrated hydrochloric acid, the solution freed from ether on the water-bath, and an excess of solid ferric chloride added. There was an immediate oily precipitate, which solidified on cooling and was crystallised from glacial acetic acid many times. It separated as greenish-yellow blades, m. p. 159—161° (Found : C, 46·4; H, 3·2; Fe, 12·6; Cl, 33·2. $C_{15}H_{11}OCl_4Fe$ requires C, 44·4; H, 2·7; Fe, 13·5; Cl, 35·05. $C_{23}H_{17}O_2Cl_4Fe$ requires C, 52·3; H, 3·25; Fe, 10·7; Cl, 27·15%).

Condensation of p-*Methoxyacetophenone and Salicylaldehyde by Hydrogen Chloride in Ether.*—Dry hydrogen chloride was passed for 2 hours into a solution of *p*-methoxyacetophenone (7·5 g.) and salicylaldehyde (6·1 g.) in dry ether (50 c.c.). After 48 hours the small orange needles were collected, washed with dry ether, dried, and extracted with 0·5% hydrochloric acid at about 40°. The flavylium chloride was partly dissolved; the greenish-yellow residue of 4'-*methoxy-4-*(p-*methoxyphenacylidene*)*flavene*, crystallised from alcohol, formed deep yellow needles (1·06 g.), m. p. 167—168° (Found : C, 78·3; H, 5·3; OMe, 16·25. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2; OMe, 16·15%).

o-*Hydroxybenzylidenedi-*(p-*methoxyacetophenone*).—A solution of *p*-methoxyacetophenone (7 g.) and salicylaldehyde (3 g.) in alcohol (30 c.c.) was treated with a hot solution of sodium hydroxide (8 g. in 8 c.c. of water). The mixture was kept over-night and then poured into water (1500 c.c.). The precipitate solidified after 2 days and was then washed with water and crystallised from alcohol, forming colourless needles (6 g.), m. p. 167° (Found : C, 74·2; H, 6·0. $C_{25}H_{24}O_5$ requires C, 74·2; H, 5·9%).

4'-*Methoxy-4-*(p-*methoxyphenacyl*)*flavene*.—The above diacetophenone (1·5 g.) was dissolved in glacial acetic acid (30 c.c.) with slight warming on the water-bath, and the solution left at room temperature for 24 hours. It was then poured into water and the yellow solid precipitated was filtered, dried, and extracted with petroleum (b. p. 60—80°). A considerable quantity of unchanged material and phenacylideneflavene remained undissolved. The pale yellow solution deposited faintly yellow needles, which were recrystallised several times from the same solvent and obtained as colourless fine needles, m. p. 122° (Found : C, 77·5; H, 5·75. $C_{25}H_{22}O_4$ requires C, 77·7; H, 5·7%).

4'-*Methoxy-4-*(p-*methoxyphenacylidene*)*flavene*.—The diacetophenone (4 g.), dissolved in glacial acetic acid (30 c.c.), was gently boiled for ¾ hour. The solution was cooled, poured into water, and steam-distilled, the residue basified with 10% caustic potash solution, and the solid product filtered off and crystallised from alcohol; it formed deep yellow needles, m. p. 167—168° and mixed m. p. with phenacylideneflavene above, 167—168°.

4'-*Methoxy-4-*(p-*methoxyphenacyl*)*flavylium Chloride*.—Through the above phenacylidene-flavene (1 g.), suspended in glacial acetic acid (10 c.c.), hydrogen chloride was passed for 3 minutes, with cooling. The red crystalline solid obtained was washed with ether and recrystallised from glacial acetic acid, forming red needles which decomposed on exposure to air and could not be analysed. M. p. 120° (decomp.). The compound was immediately decomposed in 0·5% hydrochloric acid, more slowly in 7%, reverting to the yellow phenacylideneflavene, m. p. 167°.
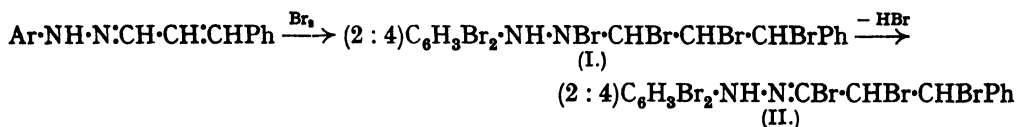
4'-*Methoxy-4-*(p-*methoxyphenacyl*)*flavylium Ferrichloride*.—This compound was obtained from the chloride prepared as above by the addition of ferric chloride (0·5 g.) in glacial acetic acid (10 c.c.) to the reaction mixture. A cloudy precipitate appeared which solidified, when scratched, after some hours. It crystallised from acetone, on addition of ether, in rosettes of fine red needles. The m. p. was indefinite, since the compound slowly decomposed on heating (Found : C, 50·8; H, 4·1; Fe, 9·2. $C_{25}H_{21}O_4Cl_4Fe$ requires C, 51·0; H, 3·6; Fe, 9·6%).

20. *The Action of Halogens upon the Arylhydrazones of Unsaturated Aldehydes.*

By F. D. CHATTAWAY and H. IRVING.

THE action of halogens upon the arylhydrazones of unsaturated aldehydes in general resembles their action upon the corresponding saturated compounds (compare Chattaway and Walker, J., 1925, **127**, 975, 1687; Chattaway and Adamson, J., 1930, 157; 1931, 2787, 2792; Chattaway, Adair, and Deighton, J., 1931, 1925). The methine hydrogen atom of the aldehyde residue is replaced, the nucleus being in no case attacked, addition of halogen to the ethylenic linkage occurs, and the aryl nucleus of the hydrazine residue is substituted, the extent of this substitution being determined by the presence or absence of substituent atoms or groups.

When, for example, 4 mols. of bromine act upon cinnamaldehydephenylhydrazone dissolved in acetic acid at the ordinary temperature, *ωαβ-tribromo-β-phenylpropaldehyde-2 : 4-dibromophenylhydrazone* (II) is produced, and the same compound results from the action of **3** mols. of bromine upon cinnamaldehyde-*p*-bromophenylhydrazone, and from the action of 2 mols. of bromine upon *cinnamaldehyde-2 : 4-dibromophenylhydrazone*. Substitution in the methine group is apparently preceded by a loose addition of halogen at the nitrogen–methine linkage, since the action of excess of bromine upon any of the three original cinnamaldehyde-hydrazones causes the formation of an unstable yellow bromine addition compound, probably of the constitution (I), which on crystallisation from acetic acid readily loses hydrogen bromide and yields the brominated hydrazone (II). Thus :
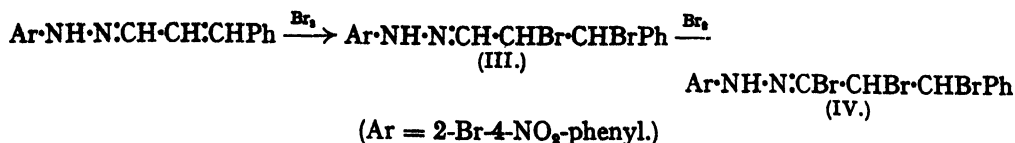
$$Ar \cdot NH \cdot N \vdots CH \cdot CH \vdots CHPh \xrightarrow{Br_4} (2:4) C_6H_3Br_2 \cdot NH \cdot NBr \cdot CHBr \cdot CHBr \cdot CHBrPh \xrightarrow{-HBr}$$
$$\text{(I.)}$$

$$(2:4) C_6H_3Br_2 \cdot NH \cdot N \vdots CBr \cdot CHBr \cdot CHBrPh$$
$$\text{(II.)}$$

(Where Ar = phenyl, *p*-bromophenyl, and 2 : 4-dibromophenyl.)

This is supported by the fact that when *cinnamaldehyde-2 : 4 : 6-tribromophenylhydrazone* is acted upon by a large excess of bromine, a similar unstable yellow addition .compound is formed which loses hydrogen bromide on crystallisation from acetic acid and yields the colourless *ωαβ-tribromo-β-phenylpropaldehyde-2 : 4 : 6-tribromophenylhydrazone*, (2 : 4 : 6)$C_6H_2Br_3 \cdot NH \cdot N \vdots CBr \cdot CHBr \cdot CHBrPh$.

In the bromination of the cinnamaldehyde-arylhydrazones no definitely preferential attack can be recognised even when less than the theoretical amount of halogen is used, since only the final fully brominated product (II) can be isolated whilst a portion of the original hydrazone is left unaltered.

The presence of a *p*-nitro-group in the phenylhydrazine residue prevents any further substitution by bromine in the nucleus, the usual reactions occurring in the aldehyde side chain only with the formation of *ωαβ-tribromo-β-phenylpropaldehyde-p-nitrophenylhydrazone* (as II).

When, however, such a nitro-group is present, the reaction can sometimes be checked at an intermediate stage. Thus, when 1 mol. of bromine is added to a solution of *cinnamaldehyde-2-bromo-4-nitrophenylhydrazone* in acetic acid at the ordinary temperature, the bromine adds on to the ethylenic linkage, no hydrogen bromide is eliminated, and *αβ-dibromo-β-phenylpropaldehyde-2-bromo-4-nitrophenylhydrazone* (III) is formed. This compound is entirely different in properties from its isomeride, *ωαβ-tribromo-β-phenylpropaldehyde-p-nitrophenylhydrazone* (above). The two hydrazones melt at 210° and 193° respectively, and whilst the latter cannot be further brominated, when 1 mol. of bromine is added to a suspension of the former (III) in acetic acid at the ordinary temperature, hydrogen bromide is evolved and *ωαβ-tribromo-β-phenylpropaldehyde-2-bromo-4-nitrophenylhydrazone* (IV) separates. Thus :

$$\text{Ar·NH·N:CH·CH:CHPh} \xrightarrow{\text{Br}_2} \text{Ar·NH·N:CH·CHBr·CHBrPh} \xrightarrow{\text{Br}_2}$$
$$\text{(III.)}$$

$$\text{Ar·NH·N:CBr·CHBr·CHBrPh}$$
$$\text{(IV.)}$$

(Ar = 2-Br-4-NO$_2$-phenyl.)

The action of chlorine upon the cinnamaldehyde-arylhydrazones resembles that of bromine, but in every case substitution in the phenyl nucleus of the hydrazine residue can be carried a stage further. Thus, when chlorine is passed through a cooled suspension in acetic acid of cinnamaldehydephenylhydrazone, of cinnamaldehyde-*p*-chlorophenylhydrazone, or of cinnamaldehyde-2 : 4-dichlorophenylhydrazone, chlorine adds on at the ethylenic linkage and substitutes in the ω-position in the aldehyde chain and in the *p*- and one *o*-position in the hydrazine nucleus (where these are not already occupied), *ωαβ-trichloro-β-phenylpropaldehyde*-2 : 4-*dichlorophenylhydrazone* (as II) being formed. Further chlorination of this compound in warm acetic acid causes substitution in the remaining *o*-position and *ωαβ-trichloro-β-phenylpropaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone*, (2 : 4 : 6)C$_6$H$_2$Cl$_3$·NH·N:CCl·CHCl·CHClPh, is formed, identical with the compound produced by the action of chlorine upon cinnamaldehyde-2 : 4 : 6-trichlorophenylhydrazone.

The action of chlorine upon cinnamaldehyde-*p*-nitrophenylhydrazone is similar, the halogen adding on at the ethylenic linkage, and substituting the methine hydrogen, but only entering one *o*-position in the hydrazine residue. The compound formed, *ωαβ-trichloro-β-phenylpropaldehyde*-2-*chloro*-4-*nitrophenylhydrazone* (as IV), also results from the chlorination of *cinnamaldehyde*-2-*chloro*-4-*nitrophenylhydrazone* under similar conditions. Direct chlorination, even in hot acetic acid solution, does not effect the introduction of another atom of chlorine into the remaining unoccupied *o*-position in the hydrazine residue, the nitro-group here, as in bromination, hindering the substitution.

EXPERIMENTAL.

The Action of Excess of Bromine upon Cinnamaldehydephenylhydrazone.—16 G. (excess) of bromine were dissolved in 10 c.c. of acetic acid and added slowly to 4·4 g. of cinnamaldehyde-phenylhydrazone (1 mol.) suspended in 20 c.c. of glacial acetic acid at the ordinary temperature. Hydrogen bromide was evolved and a yellow bromine addition compound began to separate. After 30 minutes this was collected and crystallised from boiling acetic acid ; *ωαβ-tribromo-β-phenylpropaldehyde*-2 : 4-*dibromophenylhydrazone* (II) then separated as small clusters of colourless prisms, m. p. 180° (Found : Br, 64·7. C$_{15}$H$_{11}$N$_2$Br$_5$ requires Br, 64·4%). On reduction with tin and hydrochloric acid in acetic acid solution it yielded 2 : 4-dibromoaniline, which was identified by means of its acetyl derivative.

Action of Bromine upon Cinnamaldehyde-2 : 4: 6-*tribromophenylhydrazone.*—3·2 G. of bromine in 10 c.c. of acetic acid were added slowly to 4·6 g. of cinnamaldehyde-2 : 4 : 6-tribromophenyl-hydrazone suspended in 20 c.c. of acetic acid at the ordinary temperature. Hydrogen bromide was evolved and *ωαβ-tribromo-β-phenylpropaldehyde*-2 : 4 : 6-*tribromophenylhydrazone* separated almost at once. It crystallised from acetic acid in colourless minute needles, m. p. 173° (Found : Br, 68·7. C$_{15}$H$_{10}$N$_2$Br$_6$ requires Br, 68·8%).

ωαβ-Tribromo-β-phenylpropaldehyde-p-*nitrophenylhydrazone*, prepared similarly by the action of excess of bromine upon cinnamaldehyde-*p*-nitrophenylhydrazone, crystallised from acetic acid in yellow rectangular plates, m. p. 193° (Found : Br, 47·5. C$_{15}$H$_{12}$O$_2$N$_3$Br$_3$ requires Br, 47·4%).

Action of Bromine (1 *Mol.*) *upon Cinnamaldehyde*-2-*bromo*-4-*nitrophenylhydrazone.*—1·6 G. of bromine (1 mol.) in 5 c.c. of acetic acid were added to 3·5 g. (1 mol.) of cinnamaldehyde-2-bromo-4-nitrophenylhydrazone dissolved in 200 c.c. of cold acetic acid. The coloration due to the bromine disappeared almost at once, no hydrogen bromide being evolved. On careful addition of water to the resulting clear solution, *αβ-dibromo-β-phenylpropaldehyde*-2-*bromo*-4-*nitrophenylhydrazone* (III) separated as a dark solid. It crystallised from alcohol in very dark yellow, minute prisms, m. p. 210°. This hydrazone was also synthesised directly from 3 g. of cinnamaldehyde dibromide (Zincke, *Ber.*, 1884, **17**, 1814) and 2·4 g. of *o*-bromo-*p*-nitrophenyl-hydrazine in warm acetic acid.

Action of Bromine (2 *Mols.*) *upon Cinnamaldehyde*-2-*bromo*-4-*nitrophenylhydrazone.*—4·8 G. of bromine in 10 c.c. of acetic acid were added to 3·5 g. of cinnamaldehyde-2-bromo-4-nitro-

phenylhydrazine suspended in 20 c.c. of acetic acid at the ordinary temperature. Hydrogen bromide was evolved; after 30 minutes, when the clear solution obtained was cautiously diluted with water, *ωαβ-tribromo-β-phenylpropaldehyde-2-bromo-4-nitrophenylhydrazone* (IV) separated as a solid, which crystallised from acetic acid in pale yellow, flattened, rectangular plates, m. p. 199° (Found : Br, 54·8. $C_{15}H_{11}O_2N_3Br_4$ requires Br, 54·7%).

Action of Chlorine upon Cinnamaldehydephenylhydrazone in Cold Acetic Acid.—A slow stream of chlorine was passed into a suspension of 4·4 g. of cinnamaldehydephenylhydrazone in acetic acid for 15 minutes, care being taken that the temperature did not rise above 0°. On cautious dilution of the clear, deep yellow solution which resulted, *ωαβ-trichloro-β-phenylpropaldehyde-2 : 4-dichlorophenylhydrazone* (as II) separated as a viscous yellow solid. It crystallised from acetic acid in almost colourless, hair-like needles, m. p. 158° (Found : Cl, 44·5. $C_{15}H_{11}N_2Cl_5$ requires Cl, 44·8%). On reduction with tin and hydrochloric acid in acetic acid solution it yielded 2 : 4-dichloroaniline, which was characterised by its acetyl derivative.

Action of Chlorine upon Cinnamaldehydephenylhydrazone in Warm Acetic Acid.—A rapid stream of chlorine was passed into a suspension of 4·4 g. of cinnamaldehydephenylhydrazone in 20 c.c. of acetic acid for about 20 minutes. The temperature rose to about 60° and hydrogen chloride was freely evolved. On careful addition of water to the resulting clear solution, *ωαβ-trichloro-β-phenylpropaldehyde-2 : 4 : 6-trichlorophenylhydrazone* separated as a yellow solid, which crystallised from acetic acid in colourless, short, hair-like prisms, m. p. 111° (Found : Cl, 49·3. $C_{15}H_{10}N_2Cl_6$ requires Cl, 49·4%).

This hydrazone was also obtained by the chlorination under similar conditions of cinnamaldehyde-*p*-chloro-, -2 : 4-dichloro-, and -2 : 4 : 6-trichloro-phenylhydrazone, and of *ωαβ-trichloro-β-phenylpropaldehyde-2 : 4-dichlorophenylhydrazone*. On reduction it yielded 2 : 4 : 6-trichloro-aniline.

Action of Chlorine upon Cinnamaldehyde-p-nitrophenylhydrazone.—Chlorine was passed for 20 minutes through a suspension of 5·4 g. of cinnamaldehyde-*p*-nitrophenylhydrazone in 20 c.c. of warm acetic acid. The temperature rose somewhat and hydrogen chloride was evolved. On addition of water to the resulting clear solution *ωαβ-trichloro-β-phenylpropaldehyde-2-chloro-4-nitrophenylhydrazone* separated as an orange viscous solid. It crystallised from acetic acid in deep yellow, flattened, rectangular prisms, m. p. 190°, identical with the product of chlorinating cinnamaldehyde-2-chloro-4-nitrophenylhydrazone under similar conditions (Found : Cl, 34·6. $C_{15}H_{11}O_2N_3Cl_4$ requires Cl, 34·9%).

Preparation of 2-Bromo-4-nitrophenylhydrazine.—The hydrobromide of 2-bromo-4-nitro-aniline, prepared in quantitative yield by the addition of 16 g. of bromine to a solution of 14 g. of *p*-nitroaniline in 200 c.c. of warm acetic acid (compare Korner and Contardi, *Atti R. Accad. Lincei*, 1914, **5**, 285), was made into a paste with 25 c.c. of concentrated hydrochloric acid and diazotised at 0—5° with 7 g. of sodium nitrate in 20 c.c. of water. The filtered diazonium solution was reduced with 56 c.c. of saturated ammonium sulphite and 12 c.c. of aqueous ammonia, and the yellow disulphonate which separated was digested on a water-bath with 30 c.c. of concentrated hydrochloric acid until no more sulphur dioxide was evolved (10—15 minutes). The hydrazine hydrochloride which separated on cooling was collected and dissolved in water, and the free base liberated by the addition of a concentrated aqueous solution of sodium acetate. 2-*Bromo-4-nitrophenylhydrazine* so obtained crystallised from alcohol in bright yellow needles, m. p. 142° (Found : Br, 34·65. $C_6H_6O_2N_3Br$ requires Br, 34·5%).

2-*Chloro-4-nitrophenylhydrazine*, prepared similarly, crystallised from alcohol in orange elongated plates, m. p. 140° (Found : Cl, 19·0. $C_6H_6O_2N_3Cl$ requires Cl, 18·9%).

The following hydrazones, prepared in the course of the research, have not previously been described : *cinnamaldehyde-2 : 4-dibromophenylhydrazone*, felted mass of fine yellow needles from alcohol (labile form), which changed to yellow rhombic plates (stable form), m. p. 164° (Found : Br, 42·3. $C_{15}H_{12}N_3Br_2$ requires Br, 42·0%); *cinnamaldehyde-2 : 4 : 6-tribromophenylhydrazone*, buff-coloured rectangular plates from alcohol, m. p. 125° (Found : Br, 52·0. $C_{15}H_{11}N_3Br_3$ requires Br, 52·3%); *cinnamaldehyde-2-bromo-4-nitrophenylhydrazone*, small, crimson, flattened prisms, m. p. 148° (Found : Br, 23·1. $C_{15}H_{12}O_2N_3Br$ requires Br, 23·1%); *cinnamaldehyde-2-chloro-4-nitrophenylhydrazone*, small, red, rectangular prisms, m. p. 157°, from alcohol (Found : Cl, 11·7. $C_{15}H_{12}O_2N_3Cl$ requires Cl, 11·8%).

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21. The Structure of Some Hydrocarbons related to the Sterols.

By J. D. BERNAL and (MISS) D. CROWFOOT.

THE structural formulæ of the sterols and related bile acids and œstrogenic hormones have largely been based on their dehydrogenation to polycyclic aromatic hydrocarbons (see *Ann. Reports*, 1933, **30**, 199). The formulæ are not definitely established in detail, beyond the fact that all contain a phenanthrene nucleus.

In order to elucidate doubtful points, a number of the hydrocarbons derived from sterols have been examined crystallographically by X-ray and optical methods, and compared with synthetic hydrocarbons of known structure. The general results are shown in the table. The crystals are all monoclinic or orthorhombic. Most are flat plates with

FIG. 1.
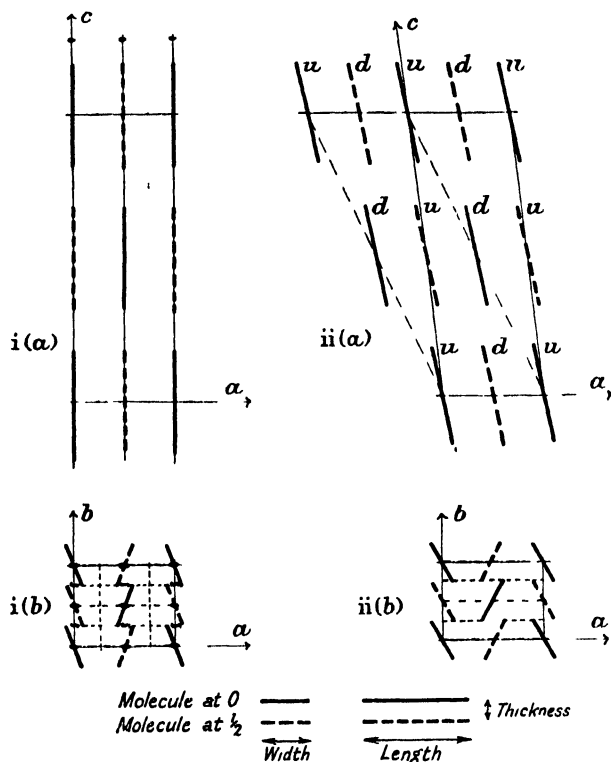
The arrangement of molecules in the hydrocarbon crystals.

i. *Orthorhombic type* (Aba) : (a) *Projection on* (010) ; (b) *projection on* (001).

ii. *Monoclinic type* (Aa) : (a) *Projection on* (010) ; (b) *projection on* (001) (*the lines - - - show the cell chosen by Iball in interpreting chrysene, orientation* 1c).

perfect cleavage in the plane of the plate, sometimes diamond-shaped, sometimes elongated along one axis. As this axis proves to be the crystallographic b axis in the monoclinic varieties (in which the elongation is most common), it is also called the b axis in the orthorhombic forms. The flat face of the crystal is chosen as the c plane, and the c axis is accordingly at right angles to it in the orthorhombic varieties and slanting at an angle β to it in the monoclinic crystals. From the crystallographically possible β values shown by the X-ray measurements, that one is generally chosen which brings c most nearly along the γ optical direction (see table). In many cases the plates as crystallised from solution were too small and imperfect for X-ray examination (though for $C_{25}H_{24}$ a crystal weighing about 10^{-6} mg. was used), but suitable crystals could always be obtained by crystallisation from the melt by the hot-wire method (Bernal and Crowfoot, *Trans. Faraday Soc.*, 1933, **29**, 1032).

	Name.		Space group.	a.	b.	c.	β.	Probable molecular length, Å.	Optic orientation.
1	Phenanthrene	C₁₄H₁₀	P2₁/a	8·66	6·11	19·24	98°	9·62	Optic axial plane (010); b = β, γ nearly along c.
2.	1 : 2-Dimethylphenanthrene	C₁₆H₁₄	Aba	8·28	6·35	21·8	90	10·9	a = α, b = β, c = γ.
3.	1 : 2 : 7-Trimethylphenanthrene	C₁₇H₁₆	Aba	7·9	6·4	24·4	90	12·2	,, ,, ,,
4.	Retene	C₁₈H₁₈	Aba	8·54	6·25	23·4	90	11·7	,, ,, ,,
5.	1 : 2-cycloPentenophenanthrene (stable)	C₁₇H₁₄	B2₁/a	18·2	6·05	21·2	119	11·6	Optic axial plane (010); b = β, γ about 6° from c.
6.	1 : 2-cycloPentenophenanthrene (metastable)	C₁₇H₁₄	Aba	8·10	6·4	22·8	90	11·4	a = α, b = β, c = γ.
7.	Diels's C₁₈H₁₆ and γ-methyl-1 : 2-cyclopentenophenanthrene	C₁₈H₁₆	Aba	8·50	6·25	24·3	90	12·1	,, ,, ,,
8.	Jacobs's C₁₈H₁₄	C₁₈H₁₄	Aba	8·2	6·35	23·7	90	11·8	,, ,, ,,
9.	"Chrysene perhydrur"	?	Aba	8·25	6·4	23·4	90	11·7	,, ,, ,,
10.	Chrysene	C₁₈H₁₂	I2/c	8·34	6·18	25·0	115·8	11·4	Optic axial plane (010); b = β, γ 10° from c in obtuse angle.
11.	2′ : 1′-Naphtha-1 : 2-fluorene	C₂₁H₁₄	Aba	7·9	6·28	26·8	90	13·4	a = α, b = β, c = γ.
12.	Ruzicka's C₂₂H₁₆ from cholic acid	C₂₂H₁₆	Aba	8·70	6·41	27·2	90	13·6	,, ,, ,,
13.	Methylcholanthrene	C₂₁H₁₆	P2₁/c	4·9	11·3	27·4	116	13·7	Optic axial plane (010); b = β, γ 27° from perpendicular to (001).
14.	1 : 2 : 5 : 6-Dibenzanthracene	C₂₂H₁₄	P2₁	7·84b	6·59a	14·17	103·5	13·75	b = a, γ perpendicular to (001).
15.	Picene	C₂₂H₁₄	Aba	8·21	6·16	28·8	90	14·4	a = α, b = β, c = γ.
16.	Ruzicka's C₂₁H₂₀ from gypsogenin	C₂₁H₂₀	P2₁	8·46	6·48	16·0	114	15·2	b = β, γ about 12° from perpendicular to (001).
17.	5-Methyl-8-isopropyl-2′ : 1′-naphtha-1 : 2-fluorene	C₂₅H₂₂	P2₁/c	13·15	8·69	30·8	96	15·9	b = β, γ 16° from perpendicular to (001).
18.	Diels's C₂₅H₂₄ from cholesterol	C₂₅H₂₄	P2₁/a	22·02	6·16	13·45	96	17·2	b = β, γ 39° from perpendicular to (001).
19.	Ruzicka's C₂₆H₂₄ from ergosterol (stable)	C₂₆H₂₄	P2₁/a	24·10	6·15	13·45	103	19·0	b = β, γ 46° from perpendicular to (001).
20.	Ruzicka's C₂₆H₂₆ from ergosterol (metastable)	C₂₆H₂₄	Pcn	15·8	6·43	39·2	90	19·6	a = α, b = β, c = γ.
21.	Ruzicka's C₂₇H₂₈ from phytosterols	C₂₇H₂₆	Pcn	13·4	7·7	39·2	90	19·6	,, ,, ,,
22.	Cholesterylene	C₂₇H₄₆	P2₁2₁2₁	15·85	7·66	19·25	90	20·5	b = β, γ
23.	Cholestane	C₂₇H₄₈	P2₁	11·2	11·0	20·5	110	20·5	b = β, γ 6° from perpendicular to (001).

Formula or probable formula
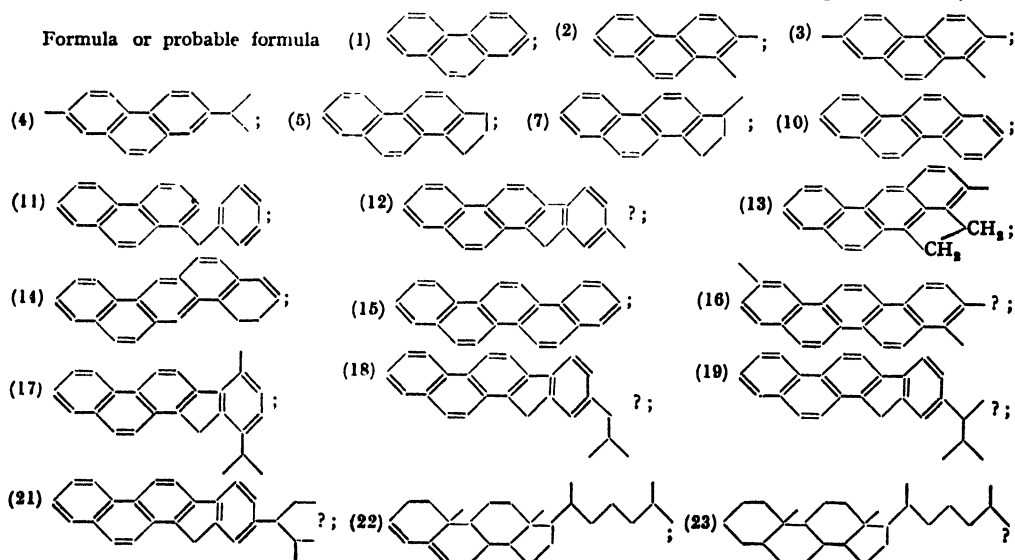
It is at once apparent that all the hydrocarbons examined, except methylcholanthrene (13) and the methyl*iso*propylnaphthafluorene (17), have in common the two cell dimensions *a* sin β and *b*, and differ in *c* according to the number of carbon atoms they contain. The optical properties indicate that the most highly refractive direction of the molecule lies along or nearly along *c* (γ), the next most refractive along *b* (β), and the least is perpendicular to (100) (α). This points to common lath-shaped molecules of width approximately 6 Å. and thickness 4 Å. packed together in parallel bundles with their lengths (γ) along the *c* axis, widths (β) along the *b*, and thicknesses (α) in the *a* planes as shown in Fig. 1. Phenanthrene, chrysene, and picene belong to the series, and we may take it to represent the mode of packing of the αβ polycyclic, condensed-ring hydrocarbons. The length of the molecule determines the *c* axis, and in the higher compounds is approximately $2.1n + 4.4$, where *n* is the number of condensed rings. The substitution of 5- for 6-carbon rings will not alter substantially the dimensions of such molecules.

Crystallographically, therefore, the table shows that the hydrocarbons appear in two characteristic forms, a monoclinic with the planes of the rings inclined to the basal *c* plane, and an orthorhombic where they are approximately parallel to it. These forms are not essentially different, as is shown by the fact that 1 : 2-*cyclo*pentenophenanthrene and Ruzicka's $C_{26}H_{26}$ crystallise in both forms, the orthorhombic being metastable.

The general arrangement of the molecules in the orthorhombic and the monoclinic form is shown in Fig. 1. Slight variations in the *a* sin β and *b* values are due either to inclination of the molecular planes to the (100) plane or to the presence of methyl or other aliphatic groups.

Tetracyclic Hydrocarbons : Diels's Hydrocarbon $C_{18}H_{16}$.—The significant hydrocarbons fall into two groups, tetracyclic and pentacyclic. The former contains *cyclo*pentenophenanthrene, $C_{17}H_{14}$, γ-methyl*cyclo*pentenophenanthrene, and the Diels hydrocarbon, $C_{18}H_{16}$. The problem of determining whether the last two are identical is very difficult, and has not yet been definitely solved.

It was relatively easy to show that the Diels hydrocarbon was not identical with *cyclo*pentenophenanthrene even in its orthorhombic form, for the spacing difference was about 1 Å. or 4% (*Chem. and Ind.*, 1933, **52**, 729). Between Diels's hydrocarbon (D) (Diels, Gädke, and Körding, *Annalen*, 1927, **459**, 1) and the two synthetic γ-*cyclo*pentenophenanthrenes prepared by different methods by Bergmann and Hilleman (B) (*Ber.*, 1933, **66**, 1302) and by Harper, Kon, and Ruzicka (K) (J., 1934, 124) no such difference could be detected. All had the same lattice dimensions within the experimental error (0.5% for *a* and *b*, 0.2% for *c*), the same relative intensities of X-ray reflexions, and the same optic axial angle, 88° ± 2°. This would normally be sufficient to establish their identity, but there were differences in chemical behaviour and in the m. p.'s of addition compounds which suggested that different compounds were involved. Consequently, a more exhaustive morphological, optical, and thermal examination was undertaken. The appearances of the hydrocarbons when crystallised under identical conditions from different solvents were definitely different : D crystallised in diamond-shaped plates, B sometimes in needles but more often in characteristic " christmas-tree " forms, K like D but with more tendency to form imperfect crystals and arborescent growths. These differences may, of course, be significant, but on the other hand they strongly suggest the presence of different impurities in all three samples.

The three sets of trinitrobenzene, trinitrotoluene, and picric acid derivatives were next examined. These were prepared for us by Dr. Kon from his own synthetic hydrocarbon, Bergmann's hydrocarbon, and from a specimen of very specially purified Diels hydrocarbon sent to us by Prof. Diels.

The trinitrobenzene compounds exist in two forms. One from solution is monoclinic, needle-shaped, elongated along (*c*), with (010) well developed and an extinction corresponding to the slow vibration 81° from *c* in the obtuse angle. No difference could be observed between the trinitrobenzene compounds of D, B, and K. From the melt, a metastable plate-like form crystallised, also monoclinic with (010) well developed but with the slow extinction direction making an angle 75° from *c* in the obtuse angle. Again no difference

could be observed. The metastable form melts some degrees below the stable, and is converted into it very slowly at temperatures near the m. p. (see below).

The trinitrotoluene compounds are triclinic and offer, therefore, far more basis for comparison. Crystallised from alcohol, they show distinct differences in habit; B appears in characteristic $\searrow \swarrow$ forms, D in lanceolate needles, often in stellate aggregates, and K is intermediate. Optical examination with the Federow instrument shows, however, that all have the same crystal form and the same direction of their optic axes.

Of all the compounds, the picrates are the most interesting because here the m. p. differences were best defined. The stable form, crystallised from alcohol, was apparently identical in all three preparations, triclinic needles twinned along their length, with the extinction angle corresponding to the optic axial plane making an angle of $8\frac{1}{4}°$ to the needle axis. The habits were, however, markedly different, the B picrate growing in separate, well-formed needles, and D and K in leafy aggregates. On melting, differences were even more marked. Both D and K picrates melted at 121—122°, whereas the recrystallised B picrate melted sharply at 128° (as against 120—122° and 130—131° observed by Kon *et al.*). On cooling, all three crystallised in a metastable leafy form, melting sharply in all cases at 117°, apparently monoclinic flattened on (010). The transformation of the metastable into the stable form takes place most readily at about 70°; at room temperatures it is extremely slow. At higher temperatures, however, characteristic differences appear, as observed by the hot-wire method. Whereas the stable form of the B picrate slowly takes the place of the metastable and grows in well-defined needles in the liquid right up to its m. p., those of the D and K picrates can never be made to replace the metastable form just below its m. p. or to grow in the liquid, for decomposition sets in before the change is complete. This suggests very strongly that the last two are not pure compounds.

All the evidence suggests that both Kon's and Bergmann's synthetic preparations and the Diels hydrocarbon are substantially identical, being probably γ-methyl*cyclo*penteno-phenanthrene, $C_{18}H_{16}$. It would seem extremely unlikely that different hydrocarbons should be indistinguishable optically and in all three unit cell dimensions, but should also each form three indistinguishable sets of addition compounds in all containing five forms. The observed differences seem to be only those of habit and m. p., and everything points to the presence of impurities, possibly in very small quantities.

Bergmann's hydrocarbon behaves more nearly as a pure compound than either of the other two. The greater resemblance between Kon's and Diels's hydrocarbons than between either of these two and Bergmann's may therefore be due to a greater proportion of impurities in these two preparations.* Differences between the impurities in the two preparations may explain why Diels (private communication) has been unable to prepare from Kon's synthetic hydrocarbon the nitroso-derivative ot which he obtained a very small yield from the natural $C_{18}H_{16}$.†

The crystal structure of the $C_{18}H_{16}$ hydrocarbons offers some points of interest. The cell is apparently orthorhombic, $8 \times 6 \times 24$ Å., and the measured density of $1·185 \pm 0·005$ indicates 4 molecules of weight 232 ± 3 (Calc. for $C_{18}H_{16}$: M, 232). The absent spectra indicate an A face-centred cell, with the probable space-group Aba (or $Abam$ if the slight pyroelectricity found is not a genuine effect). In this space-group, each molecule must possess an axis of symmetry. As no suggested chemical formula for $C_{18}H_{16}$ can give an axis of symmetry, we are consequently forced either (*a*) to lower the space-group to monoclinic Aa (or $A2/a$), $\beta = 90°$, without any evidence of difference of intensities between $(h\,k\,l)$ and $(h\,k\,\bar{l})$, (*b*) to assume a statistical distribution of molecules, or (*c*) to imagine the crystal built of monoclinic units repeatedly twinned on (001) so as to make the c axis a pseudo-dead axis (Fig. 2). The last alternative seems the most probable, but further work on larger and better-formed crystals will be necessary to confirm it. The tendency to

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* (Note added in proof.) The question of the purity of Diels's hydrocarbon has been recently discussed by H. W. Thompson (*Chem. and Ind.*, 1934, **53**, 1027) and J. W. Cook (*ibid.*, p. 1047).

† (Note added in proof.) H. Hilleman has since prepared this nitroso-derivative from his own and Bergmann's preparation (*Ber.*, 1935, **68**, 102), so doubt on this score at least as to the substantial identity of the compounds is removed.

statistical symmetry, which is present in any case, probably explains the frequent occurrence of this type among the condensed-ring hydrocarbons (see Table, Nos. 2, 3, 4, 6, 7, 8, 9, 11, 12, 15) and also the extreme ease with which they form solid solutions with each other, with the consequent difficulty in purification by ordinary methods.

The physical structure of the crystals, however, is clear enough; the analogies to chrysene and to the hydrocarbon $C_{25}H_{20}$ (probably a trimethylpicene) prepared from gypsogenin (Ruzicka, Hösli, and Ehmann, *Helv. Chim. Acta*, 1934, **17**, 442), as well as the optical properties and the strength of the (200) plane, all point to the typical arrangement shown in Fig. 2, the length of the molecule being nearly exactly along *c*, the width not so near to *b*, and the thickness to *a*.

To the C_{18} type belong a number of other hydrocarbons examined, notably 1 : 2-dimethyl- and 1 : 2 : 7-trimethyl-phenanthrene (2 and 3), retene (4) which is extremely similar to Diels's $C_{18}H_{16}$ (7), and Jacobs and Fleck's $C_{16}H_{14}$ (8) (*J. Biol. Chem.*, 1932, **97**, 57). The intermediate *c* spacing of the last, *viz.*, 23·4 Å., might well result from its being a mixed crystal of a compound similar to (2) and (7), which would agree well with Jacobs's later conclusions that this is not a pure compound but a mixture of Diels's $C_{18}H_{16}$ and a dimethylphenanthrene. The obscure compound " chrysene perhydrur " (9) (von Braun and Irmisch, *Ber.*, 1932, **65**, 883) is practically indistinguishable from this and may also be a mixture; further work on this compound would probably throw light on the nature of Diels's hydrocarbon.

Finally, the complete solution of the structure of chrysene (Iball, *Proc. Roy. Soc.*, 1934, **146**, 153) is a satisfactory check on the correctness of the rougher methods used by us in arriving at the structure of the other hydrocarbons.

Pentacyclic Hydrocarbons.—The first point of interest here is the nature of the hydrocarbon $C_{21}H_{16}$ (12) obtained from cholic acid by Ruzicka, Thomann, Brandenburger, Furter, and Goldberg (*Helv. Chim. Acta*, 1933, **17**, 200). It can be seen that it fits into the typical orthorhombic series, lying between naphthafluorene (11) and picene (15). The formula suggested for it by Ruzicka (private communication) is (I), but this seems
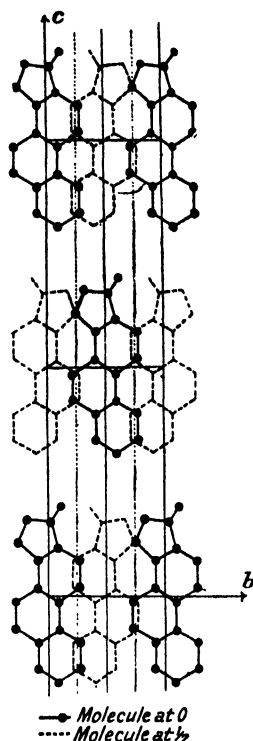
FIG. 2.

—• *Molecule at* 0
·····*Molecule at ½*

Diagram to illustrate the crystal structure of γ-methylcyclopentenophenanthrene projected on (100). *The unit shown belongs to the space-group* Aa. *To obtain a structure simulating* Aba, *such units may be imagined to be combined in groups by twinning, or individual molecules may, while still occupying the same general positions, be turned statistically to the right and left throughout the structure instead of regularly as in the figure.*
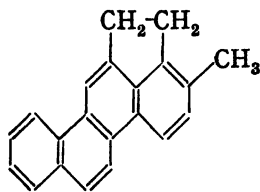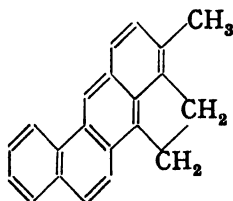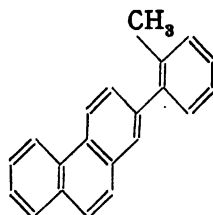
(I.)   (II.)   (III.)

improbable in view of the totally different structure of methylcholanthrene (13) (II) (Wieland and Dane, *Z. physiol. Chem.*, 1933, **219**, 240; Cook and Haslewood, *J.*, 1934, 428). The crystal structure of this compound as indicated by the table is markedly different from that of all the other hydrocarbons examined, as might be expected from its

possessing three rings sharing one carbon atom. It crystallises in needles, and resembles in most ways the flat molecule rather than the long-chain hydrocarbons. It seems probable that $C_{21}H_{16}$, on the other hand, is one of the latter type, but it is difficult to suggest a formula for it different from that of naphthafluorene. It may possibly be a methyl-naphthadiphenyl, $C_{21}H_{16}$ (III), but the density, $1 \cdot 244 \pm 0 \cdot 002$, suggests that the molecular weight is higher than that required by the formula $C_{21}H_{16}$ and closely in agreement with the formula $C_{22}H_{18}$. Although this needs confirmation by more accurate X-ray work, the possibility remains that the compound may be a methylnaphthafluorene.

Far more important, however, for the study of the mechanism of dehydrogenation of the sterols are the hydrocarbons, $C_{25}H_{24}$, first obtained from cholesterol by Diels (*loc. cit.*), and $C_{26}H_{26}$ and $C_{27}H_{28}$, prepared by Ruzicka *et al.* from ergosterol and from a mixture of phytosterols respectively (*Helv. Chim. Acta*, 1933, **17**, 200). As the formulæ of these three compounds have given rise to much dispute, it seemed important to make a complete study. [$C_{25}H_{24}$ had been examined in 1932, but as only extremely small crystals (*ca.* 10^{-6} mg.) were available it was impossible to be certain of the results, though they have since been confirmed.]

FIG. 3.

. *Molecule at 0*
. *Molecule at ½*
✗ *Centre of symmetry at ¼, ¾.*
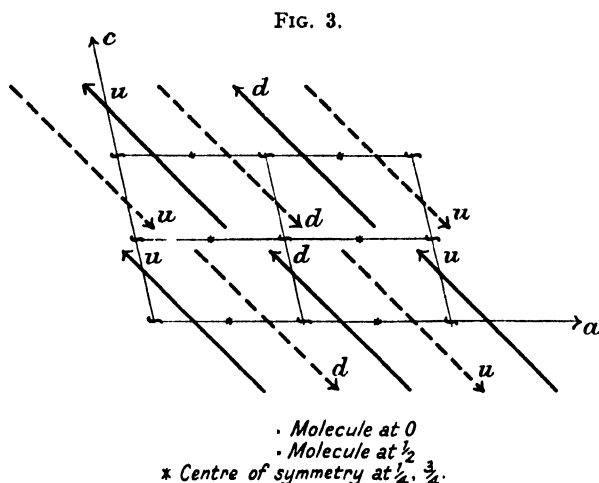
Molecular arrangement in the monoclinic form of $C_{26}H_{26}$.

$C_{25}H_{24}$ and $C_{26}H_{26}$ crystallise from solution in similar but distinct forms. Both are lath-shaped, monoclinic crystals elongated along b, but the faces are much better developed in the second compound. The cell dimensions (see table), together with the observed densities, *viz.*, $1 \cdot 195 \pm 0 \cdot 003$ and $1 \cdot 158 \pm 0 \cdot 003$, lead to cells containing 4 molecules of molecular weights 327 ± 7 and 341 ± 5, respectively (Calc. : 324, 338, respectively). Thus there can no longer be any doubt that the numbers of carbon atoms in the molecules are correctly assigned. The positions of the molecules in the cell are fixed by the direction of the highest vibration direction γ; they make angles 39° and 46° respectively to the normal to the c plane. From these and the cell dimensions, the lengths of the molecules can be determined as 17·2 and 19·0 Å., respectively (see Fig. 3). From the melt, $C_{25}H_{24}$ recrystallises in the same form, but $C_{26}H_{26}$ on rapid cooling shows a metastable, plate-like, orthorhombic variety (20), with the molecules parallel to the c axis and a crystal structure rather more complicated than, but essentially similar to, that of $C_{18}H_{16}$. The value of the axial length c, 39·2 Å. ($2 \times 19 \cdot 6$), confirms the values found from the monoclinic variety.

$C_{27}H_{28}$ crystallises directly from solution in small diamond-shaped plates which are orthorhombic or pseudo-orthorhombic and show exactly the same type of arrangement as that found in the metastable orthorhombic variety of $C_{26}H_{26}$. The length of c, which defines the length of the molecules, is $2 \times 19 \cdot 6$ Å., very little different from that found for $C_{26}H_{26}$, but there are marked differences in the a and b dimensions and in the intensities of the various planes. The crystal structures of the two hydrocarbons $C_{26}H_{26}$

the antimerides, the unesterified acid was dextrorotatory, whereas *r*-mandelic acid under similar experimental conditions gives a lævorotatory acid.

Our experience on the reduction of *r-o*-nitromandelic acid either with zinc and acetic acid or with tin and hydrochloric acid held out little hope that such methods, involving as they do the use of an acid medium, would be of service when applied for the preparation of the optically active dioxindoles.

(—)*o*-Nitromandelic acid was accordingly reduced by ferrous sulphate and baryta in the manner outlined for the *r*-isomeride. The sodium salt of the amino-acid was lævorotatory in water and gave the (—)*amino*-acid. A change of sign of rotation took place when the salt was decomposed by additional mineral acid, the product being (+)*dioxindole*. Under the conditions described in the experimental section the change required 29 hours at the ordinary temperature. By the similar procedure, (+)o-*aminomandelic acid* and (—)*dioxindole* were prepared.

The rotation of (—)*o*-aminomandelic acid in *N*-hydrochloric acid fell from $[\alpha]_{5461} - 151°$ to zero when the solution was kept at the ordinary temperature for 312 hours. Since isatide was then isolated, it was clear that the (—)*o*-amino-acid was first transformed into (+)dioxindole, which was oxidised to isatide. Heller (*loc. cit.*) mentions that *r*-dioxindole is transformed into isatide by hydrochloric acid, and we have observed that isatide is also formed from *r-o*-aminomandelic acid in the presence of hydrochloric acid.

The optically active dioxindoles are prone both to decomposition and to racemisation, and with the exception of the antimeric *N*-hydroxydioxindoles we have not obtained any derivatives of them where the optical activity was retained. Thus, the action of phenylhydrazine on the (+)antimeride gave isatin-β-phenylhydrazone, whilst acetyl chloride gave *r-O*-acetyldioxindole, and benzoyl chloride gave *r*-dibenzoyldioxindole. Even a few drops of alcoholic potash (0·5*N*) added to an ethyl-alcoholic solution brought about almost at once the disappearance of rotatory power with the formation of isatide. With less alcoholic potash, however, a gradual fall of rotatory power was observed (see experimental section). The addition of further alkali caused the precipitation of a white solid, which was probably the potassium derivative of *r*-dioxindole. Pyridine also caused the complete racemisation of (+)dioxindole.
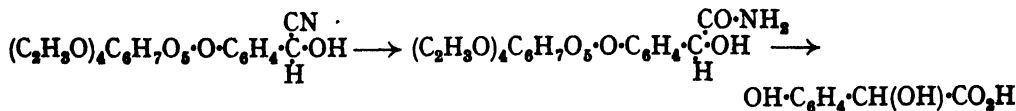
It seems likely enough that the fall in rotatory power observed with a trace of alcoholic potash might have been due to the migration of a hydrogen atom to the oxygen atom of the adjacent carbonyl group with the formation of enolic dioxindole, which contains no asymmetric carbon atom, thus :
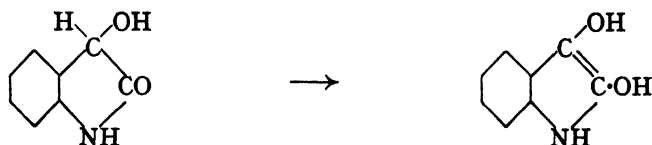
An interesting point arose when a trace of alcoholic potash was added to an ethyl-alcoholic solution of *r*-dioxindole. It was impossible to recover the *r*-dioxindole, isatide being obtained instead, whereas *r*-dioxindole can be recovered from its ethyl-alcoholic solution in the absence of alcoholic potash. The deduction which we draw from these observations is that the trace of alcoholic potash acts catalytically to form enolic dioxindole (Baeyer's " Hydroisatin "), which then undergoes oxidation readily to isatide. Again, the dioxindoles melt indefinitely, since they undergo transformation into isatide on rise of temperature; it seems probable that here also enolic dioxindole is formed as an intermediate phase.

One of the early attempts to realise an asymmetric synthesis had helicin as its starting point (E. Fischer and Slimmer, *Sitzungber. K. Akad. Wiss. Berlin*, 1902, **28**, 597; *Ber.*, 1903, **36**, 2575). Hydrogen cyanide combined quantitatively with tetra-acetylhelicin to form a crystalline cyanohydrin which had all the appearance of uniformity and had thus apparently been formed by an addition which was entirely one-sided. But this is not an asymmetric synthesis in the sense of the term as used by Fischer, Marckwald, McKenzie,

and others. This cyanohydrin was then converted into the amide, which was hydrolysed by dilute hydrochloric acid to give *o*-hydroxymandelic acid :

$$(C_2H_3O)_4C_6H_7O_5 \cdot O \cdot C_6H_4 \cdot \underset{H}{\overset{CN}{\underset{|}{\overset{|}{C}}}} \cdot OH \longrightarrow (C_2H_3O)_4C_6H_7O_5 \cdot O \cdot C_6H_4 \cdot \underset{H}{\overset{CO \cdot NH_2}{\underset{|}{\overset{|}{C}}}} \cdot OH \longrightarrow$$

$$OH \cdot C_6H_4 \cdot CH(OH) \cdot CO_2H$$

The rotatory power of the hydroxy-acid obtained in this manner was so small that Fischer and Slimmer did not claim to have effected an asymmetric synthesis. The highest value quoted for a product which was not analysed was $[\alpha]_D^{20°} + 1.9°$ in ether, but unfortunately the observed angle of rotation is not recorded. It may justifiably be assumed, however, that the solution examined gave so small an angle of rotation that evidence for optical activity could not be accepted as definite.

In the light of these experiments the isolation of optically active *o*-hydroxymandelic acid from sodium (—)*o*-aminomandelate was of some interest. The value in ether was $[\alpha]_D^{18°} - 53.8°$.

The reduction of (+)*o*-nitromandelic acid by zinc dust and ammonium hydroxide was accompanied by a change of sign of rotation, the product being (—)*N*-hydroxydioxindole :
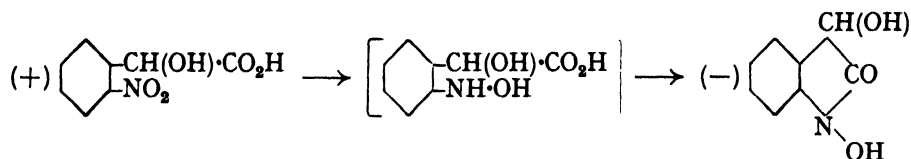
The antimeric (+)*N*-hydroxydioxindole was isolated in a similar manner.

EXPERIMENTAL.

The method outlined by Heller and Spielmeyer (*Ber.*, 1925, **58**, 834) for the preparation of *r-o*-nitromandelonitrile was found to be more satisfactory than those previously described (Heller, *Ber.*, 1904, **37**, 938; 1906, **39**, 2334; Reissert and Hessert, *Ber.*, 1924, **57**, 964). The following procedure is convenient for the preparation of *r-o*-nitromandelic acid.

o-Nitrobenzaldehyde (50 g.) was suspended in glacial acetic acid (100 g.) kept at 0°, and a solution of potassium cyanide (33 g.) in water (66 c.c.) was gradually added. After 4—5 hours, sufficient water was added to complete the separation of the crystals, which were removed and hydrolysed by concentrated hydrochloric acid. The *r-o*-nitromandelic acid obtained, crystallised from water, formed colourless prisms (48 g.), m. p. 137—138°.

Reduction of r-o-*Nitromandelic Acid.*—(a) *With zinc and acetic acid.* This reaction (Heller, *Ber.*, 1904, **37**, 938) was in our hands unsatisfactory; *e.g.*, only about 0·3 g. of pure *r*-dioxindole (prisms from water) was obtained from 5 g. of the acid. Our product was identical with a specimen obtained by the reduction of isatin with sodium hydrosulphite (Marschalk, *Ber.*, 1912, **45**, 582). In accordance with Heller's observations, *r*-dioxindole is readily oxidised in aqueous solution to form isatide. *r*-Dioxindole melts indefinitely at about 170° with preliminary softening; the molten mass readily absorbs oxygen, becoming solid and then giving the m. p. of isatide.

(b) *With tin and hydrochloric acid.* *r-o*-Nitromandelic acid (10 g.) was warmed with concentrated hydrochloric acid (60 c.c.) and granulated tin (20 g.); *r*-dioxindole hydrochloride (3 g.), m. p. 156° (decomp.), was isolated after removal of the tin as sulphide (Found : Cl, 18·7. Calc. for $C_8H_7O_2N,HCl$: Cl, 19·1%). When the hydrochloride was crystallised thrice from water, it was transformed into *r*-dioxindole.

(c) *With ferrous sulphate and barium hydroxide.* 300 C.c. of a warm aqueous solution of barium *r-o*-nitromandelate, prepared by neutralising 30 g. of the acid with barium hydroxide, were added to a warm solution of ferrous sulphate (275 g.) in water (255 c.c.). After the addition of a warm solution of barium hydroxide (330 g.) in water (1 l.), the mixture was stirred for 1 hour, boiled for ½ hour, and filtered hot. On cooling, plates of barium *r-o*-aminomandelate separated, and a further quantity of this salt was obtained by boiling the residue thrice with water, precipitating the excess of barium hydroxide as carbonate, and concentrating the liquors. The barium *r-o*-aminomandelate (22 g.) was converted into the sodium salt by boiling with the

calculated quantity of sodium carbonate and then removing the barium carbonate. The aqueous solution of the sodium salt was decomposed at 40° by slightly less than the calculated quantity of dilute sulphuric acid; the amino-acid (11 g.) then separated.

r-o-*Aminomandelic acid* forms prisms, m. p. 144° (decomp.) (Found : C, 57·7; H, 5·5. $C_8H_9O_3N$ requires C, 57·5; H, 5·4%).

When the sodium salt was acidified at 40° by dilute sulphuric acid containing twice the amount necessary for decomposition, the needles which were deposited in 82% yield gave in ethyl-alcoholic solution a faint transient violet coloration on the addition of ammonia. When the needles were moistened with hot barium hydroxide, they assumed a violet coloration which was slowly evanescent. These colour reactions as well as the m. p. were identical with the behaviour of an authentic specimen of r-dioxindole.

When a solution of r-o-aminomandelic acid in an excess of dilute hydrochloric acid was evaporated under diminished pressure at the ordinary temperature, a solid, m. p. 243—246° (decomp.), separated, which in pyridine gave a violet coloration with barium hydroxide, and a ruby-red coloration on heating with ethyl alcohol–sodium carbonate. When shaken with concentrated sulphuric acid and benzene, it caused the sulphuric acid to assume a green coloration. This solid was isatide.

By acetylation in cold aqueous suspension with acetic anhydride, r-o-aminomandelic acid gave r-o-*acetamidomandelic acid*, crystallising from water in needles, m. p. 142—143° (Found : C, 57·6; H, 5·5. Calc. for $C_{10}H_{11}O_4N$: C, 57·4; H, 5·3%). It gave no depression in m. p. on admixture with an authentic specimen prepared by converting N-acetylisatin (Camps, *Arch. Pharm.*, 1899, **237**, 587) into acetylisatinic acid (Aeschlimann, J., 1926, 2907), and reducing the latter by sodium amalgam (Suida, *loc. cit.*).

r-o-*Benzamidomandelic acid*, prepared by benzoylating sodium r-o-aminomandelate by benzoyl chloride and caustic soda, crystallised from benzene–ethyl alcohol in needles, m. p. 146° (Found : C, 66·4; H, 5·0. $C_{15}H_{13}O_4N$ requires C, 66·4; H, 4·8%). It was also formed from r-dioxindole (2 g.) by boiling under reflux for 1 hour with 2N-caustic soda (25 c.c.), cooling, and then benzoylating with benzoyl chloride (6 g.). The main product was the benzoyl acid; another substance, m. p. 217°, formed in small quantity, was not further examined.

r-o-β-*Naphtholazomandelic acid*, prepared from sodium r-o-aminomandelate by diazotisation and coupling of the diazonium solution with β-naphthol, crystallised from glacial acetic acid in red needles, m. p. 205—206° (decomp.) (Found : C, 66·9; H, 4·4. $C_{18}H_{14}O_4N_2$ requires C, 67·1; H, 4·4%).

Reduction of r-o-*Nitroacetylmandelic Acid.*—r-o-Nitromandelic acid was acetylated by acetyl chloride to give r-o-*nitroacetylmandelic acid*, separating from chloroform–light petroleum (b. p. 60—80°) in colourless prisms, m. p. 102—103° (Found : C, 50·0; H, 3·8. $C_{10}H_9O_6N$ requires C, 50·2; H, 3·8%). Reduction with various reagents was unsuccessful, except with zinc dust and glacial acetic acid, which gave O-acetyldioxindole but unfortunately in very small yield. The reduction of (+)o-nitroacetylmandelic acid, m. p. 95—96° (p. 108), was not attempted.

r-o-*Nitrophenylmethoxyacetic Acid.*—An intimate mixture of r-o-nitromandelic acid (8·5 g.) and dry silver oxide (20 g.) was added gradually with cooling to methyl iodide (34·5 g.), and the reaction completed by heating for 1 hour on the water-bath. The oil (8·7 g.) isolated was saponified with a solution of potassium hydroxide (4·4 g.) in water (30 c.c.). r-o-*Nitrophenylmethoxyacetic acid* (dried under diminished pressure at 60°) crystallised from water in plates, m. p. 81—82°. Yield, 8 g. (Found : C, 51·0; H, 4·5. $C_9H_9O_5N$ requires C, 51·2; H, 4·3%).

Ethyl r-o-*Nitrobenzoylmandelate.*—Benzoyl chloride (18 c.c.) was added gradually to a solution of ethyl r-o-nitromandelate (10 g.) in pyridine (50 g.) kept at 0°. After addition of dilute hydrochloric acid the resulting ethyl r-o-nitrobenzoylmandelate separated from ethyl alcohol–light petroleum (b. p. 60—80°) as rectangular prisms (11·5 g.), m. p. 76—77° (Found : C, 62·0; H, 4·7. Calc. for $C_{17}H_{15}O_6N$: C, 62·0; H, 4·6%). Heller (*Ber.*, 1906, **39**, 2334) obtained this compound by a different method.

The reduction of ethyl r-o-nitrobenzoylmandelate with stannous chloride and hydrochloric acid gave O-benzoyldioxindole in 83% yield.

Resolution of r-o-*Nitromandelic Acid.*—100 G. of brucine (1 mol.) were added with stirring to a hot solution of 50 g. of the acid (1 mol.) in water (2 l.). After 16 hours, crystals (A, 68 g.) had separated, and from the filtrate crystals (B, 60 g.) were deposited after 36 hours longer. On crystallising A thrice from water, the homogeneous brucine (—)o-nitromandelate (46 g.) crystallised with $4H_2O$ as hexagonal plates (m. p. 91—92°), which after heating under diminished pressure at 80° had m. p. 137° (decomp.) and then gave in acetone ($l = 2$, $c = 2·4305$) $\alpha_{5461}^{20·5°}$ — 16·63°, $[\alpha]_{5461}^{20·5°}$ — 342°. The brucine was removed by precipitating the aqueous solution

of this salt with ammonia, the filtrate being then acidified by hydrochloric acid. The resulting acid, obtained by extraction with ether, was crystallised once from chloroform, yielding 13 g. of (—)-*o-nitromandelic acid* in colourless hexagonal plates, m. p. 100—101° (Found : C, 48·5; H, 3·7. $C_8H_7O_5N$ requires C, 48·7; H, 3·6%). Its rotatory power was determined in acetone ($l = 2$, $c = 1.5785$, $t = 20°$) :

λ	6708	6563	5893	5461	4861	4358
α	− 10·21°	− 10·89°	− 14·79°	− 18·74°	− 28·90°	− 48·35°
[α]	− 323°	− 345°	− 468°	− 594°	− 915°	−1532°

In acetone ($l = 2$, $c = 1.8955$), $\alpha_{5791}^{20°} - 18.56°$, $[\alpha]_{5791}^{20°} - 490°$.

The three successive filtrates from which A had been crystallised gave acids with $[\alpha]_{5791}$ − 268°, − 473°, and − 483° respectively in acetone ($c = 2$) after removal of the brucine.

Crystallisation of B thrice from water gave the homogeneous brucine (+)-*o*-nitromandelate, needles (35 g.) which when dried in air contained $2H_2O$. When dried under diminished pressure at 80°, it had m. p. 137° (decomp.). In acetone ($l = 2$, $c = 2.336$), $\alpha_{5461}^{20°} + 13.61°$, $[\alpha]_{5461}^{20°} + 291°$.

(+)-*o-Nitromandelic acid* from the brucine salt crystallised from chloroform in colourless hexagonal plates, m. p. 100—101° (Found : C, 48·9; H, 3·8. $C_8H_7O_5N$ requires·C, 48·7; H, 3·6%). Yield, 10 g. The rotation in acetone was in agreement with that for its antimeride ($l = 2$, $c = 1.896$) : $\alpha_{5791}^{20°} + 18.59°$, $[\alpha]_{5461}^{20°} + 490°$. The rotatory power decreases with rise of temperature : in acetone ($l = 2$, $c = 1.8965$),

λ.	$\alpha^{1.5°}$.	$[\alpha]^{1.5°}$.	$\alpha^{20°}$.	$[\alpha]^{20°}$.	$\alpha^{40°}$.	$[\alpha]^{40°}$.
5461	+23·92°	+ 631°	+22·54°	+ 594°	+21·14°	+ 557°
4358	+62·67	+1652	+58·54	+1543	+54·86	+1446

The three successive filtrates from which B had been crystallised gave acids with $[\alpha]_{5791}$ + 256°, + 444°, and + 477° respectively in acetone ($c = 2$).

(+)-*o-Nitroacetylmandelic acid*, prepared by acetylating (+)-*o*-nitromandelic acid with acetyl chloride, formed colourless prisms, m. p. 95—96°, from benzene (Found : C, 50·1; H, 3·8. $C_{10}H_9O_6N$ requires C, 50·2; H, 3·8%). In acetone ($l = 2$, $c = 2.09$), $\alpha_D^{20.5°} + 12.10°$, $[\alpha]_D^{20.5°} + 289°$; $\alpha_{5461}^{20°} + 15.34°$, $[\alpha]_{5461}^{20°} + 367°$.

Ethyl (+)-*o-nitromandelate*, prepared from the (+)-acid, is a pale yellow oil, b. p. 165—166°/4 mm. (Found : C, 53·2; H, 5·1. $C_{10}H_{11}O_5N$ requires C, 53·3; H, 4·9%), whereas the isomeric *r*-ester is a solid, m. p. 49—50° (Heller, *Ber.*, 1904, 37, 938). In acetone ($l = 2$, $c = 2.9645$), $\alpha_D^{20.5°} + 17.91°$, $[\alpha]_D^{20.5°} + 302°$; $\alpha_{5461}^{20°} + 22.78°$, $[\alpha]_{5461}^{20°} + 384°$. In pyridine ($l = 2$, $c = 2.9385$), $\alpha_{5461}^{18.5°} + 17.75°$, $[\alpha]_{5461}^{18.5°} + 302°$. When the latter solution was kept for 9 days at the ordinary temperature, the rotatory power remained unaltered. The ester itself became dark-coloured on keeping.

Fractional Esterification of r-o-Nitromandelic Acid by (—)*Menthol.*—The *r*-acid (6 g.) was esterified at 150—155° by (—)-menthol (6 g.) for 1¼ hours. The ethereal solution of the product was shaken with sodium bicarbonate. The unesterified acid (2·4 g.) obtained from the alkaline solution by acidification with hydrochloric acid and extraction with ether was dextrorotatory in acetone ($l = 2$, $c = 7.3065$), $\alpha_{5461}^{20.5°} + 4.3°$, $[\alpha]_{5461}^{20.5°} + 29.4°$.

The Optically Active o-Aminomandelic Acids.—(—)-*o-Aminomandelic acid.* (—)-*o*-Nitro-mandelic acid (7·5 g.) was reduced with barium hydroxide and ferrous sulphate as described for the *r*-isomeride to form barium (—)-*o*-aminomandelate (7·6 g.), which is considerably more soluble in water than is the *r*-salt. This salt was then converted into the sodium salt, which is very soluble in water and crystallises in rectangular plates. (—)-*o-Aminomandelic acid*, obtained by decomposing the sodium salt with dilute sulphuric acid in an amount slightly less than that calculated for 1 mol. of salt, crystallises from water in prisms, m. p. 159° (decomp.) (Found : C, 57·6; H, 5·6. $C_8H_9O_3N$ requires C, 57·5; H, 5·4%). In *N*-caustic soda ($l = 1$, $c = 1.63$, $t = 20°$) :

λ	6708	6563	5893	5791	5461	5106	4861	4358
α	− 1·87°	− 2·01°	− 2·61°	− 2·85°	− 3·18°	− 3·84°	− 4·14°	− 5·54°
[α]	−115°	−123°	−160°	−175°	−195°	−236°	−254°	−340°

In ammonium hydroxide (0·95N) ($l = 1$, $c = 1.227$): $\alpha_{5461}^{20°} - 2.34°$, $[\alpha]_{5461}^{20°} - 191°$; $\alpha_{5791}^{20°} - 2.08$, $[\alpha]_{5791}^{20°} - 170°$.

In *N*-hydrochloric acid ($l = 1$, $c = 1.954$): $\alpha_{5461}^{16°} - 2.96°$, $[\alpha]_{5461}^{16°} - 151°$. This solution gradually lost its optical activity when kept at 16° :

Hours	19½	43½	67½	163	312
α_{5461}	−0·41°	−0·15°	−0·09°	−0·04°	0·00°

From the resulting solution a colourless, sparingly soluble substance separated. It had m. p. 243—245° (decomp.), gave a violet coloration when barium hydroxide was added to its solution in pyridine, and an evanescent ruby-red coloration on heating with ethyl alcohol–sodium carbonate. These properties are exhibited by isatide.

Finely powdered (−)o-aminomandelic acid (1·2 g.) was suspended in water (16 c.c.) and then shaken at 0° with acetic anhydride (1·5 c.c.) until it had all dissolved. (−)o-*Acetamidomandelic acid* (0·8 g.) separated from benzene–acetone in needles, m. p. 160° (Found : C, 57·2; H, 5·5. $C_{10}H_{11}O_4N$ requires C, 57·4; H, 5·3%). In acetone ($l = 2$, $c = 1·0325$), $\alpha_D^{20°} - 3·89°$, $[\alpha]_D^{20°} - 188°$, $[\alpha]_{5461}^{20°} - 4·69°$, $[\alpha]_{5461}^{20°} - 227°$.

(−)o-β-*Naphtholazomandelic acid*, prepared from sodium (−)o-aminomandelate by diazotisation and coupling of the diazonium solution with β-naphthol, crystallised from glacial acetic acid in red needles, m. p. 190—191° (decomp.) (Found : C, 66·7; H, 4·5; N, 9·1. $C_{18}H_{14}O_4N_2$ requires C, 67·1; H, 4·4; N, 8·7%).

(+)o-*Aminomandelic acid*, prepared from sodium (+)o-aminomandelate, formed prisms, m. p. 159° (decomp.) (Found : C, 57·6; H, 5·6. $C_8H_9O_3N$ requires C, 57·5; H, 5·4%). In ammonium hydroxide ($0·95N$) ($l = 1$, $c = 1·178$), $\alpha_{5461}^{20°} + 2·24°$, $[\alpha]_{5461}^{20°} + 190°$. In pyridine ($l = 1$, $c = 2·685$), $\alpha_{5461}^{17°} + 6·92°$, $[\alpha]_{5461}^{17°} + 258°$; $\alpha_{5791}^{17°} + 5·98°$, $[\alpha]_{5791}^{17°} + 223°$.

The latter solution gradually dropped in dextrorotatory power and finally became lævorotatory. It became gradually reddish-brown, and polarimetric readings could not eventually be taken for λ_{5461} and λ_{5791}. The readings for λ_{6563} are only approximate, but the lævorotation seems to remain constant after 270 hours.

Hours	5	70½	95½	119	145		
$[\alpha]_{5461}$	+254°	+182°	+144°	+110°	—		
$[\alpha]_{5791}$	+220°	+162°	+134°	+ 99°	+ 66°		
Hours	167	174	241	246½	264¼	270	287
$[\alpha]_{5791}$	+ 44°	+ 31°	—	—	—	—	—
$[\alpha]_{6563}$	+ 37°	+ 37°	− 5°	− 24°	− 28°	− 45°	− 45°

The residue obtained after removal of the pyridine was lævorotatory in ethyl alcohol.

Action of Dilute Sulphuric Acid on (−)o-*Aminomandelic Acid.*—0·1755 G. of the acid (1 mol.) was made up to 10 c.c. with dilute sulphuric acid (¼ mol.) : $l = 1$, $c = 1·755$, $\alpha_{5461}^{16°} - 2·48°$, $[\alpha]_{5461}^{16°} - 141°$. The solution gradually changed its sign of rotation from lævo to dextro :

Time	8 (mins.)	18	40	2 (hrs.)	4	6	23	26	29	48
$\alpha_{5461}^{16°}$	−2·45°	−2·39°	−2·24°	−1·72°	−1·10°	−0·70°	+0·37°	+0·43°	+0·50°	+0·50°

When the rotatory power had reached a constant value, (+)dioxindole was isolated from the solution.

(+)*Dioxindole.*—A solution of 3·4 g. of sodium (−)o-aminomandelate (1 mol.) in 25 c.c. of water was acted upon at 30° by 14·4 c.c. of dilute sulphuric acid containing twice the amount necessary for the decomposition of the sodium salt. Precautions should be taken to prevent oxidation. After 1 day at the ordinary temperature under diminished pressure, optically pure (+)dioxindole (1·1 g.) separated. (+)*Dioxindole* gives in ethyl-alcoholic solution a faint transient violet coloration on the addition of ammonia. When (+)dioxindole was moistened with hot barium hydroxide, it assumed a pronounced violet coloration. It crystallises from water in prisms which when heated rapidly have m. p. 167—168° with preliminary softening (Found : C, 64·2; H, 5·0. $C_8H_7O_2N$ requires C, 64·4; H, 4·7%). In acetone ($l = 1$, $c = 2·099$), $\alpha_{5461}^{20°} + 0·84°$, $[\alpha]_{5461}^{20°} + 40°$; $\alpha_D^{20°} + 0·71°$, $[\alpha]_D^{20°} + 34°$. In ethyl alcohol ($l = 1$, $c = 1·964$), $\alpha_{5461}^{20·5°} + 1·09°$, $[\alpha]_{5461}^{20·5°} + 55·5°$; $\alpha_{5791}^{20·5°} + 1·0°$, $[\alpha]_{5791}^{20·5°} + 51°$. The solution in acetone did not change in rotatory power after several days, but when it was kept in a closed flask for a few weeks, isatide gradually separated from it.

(−)*Dioxindole*, prepared from sodium (+)o-aminomandelate, forms prisms, m. p. 167—168° with preliminary softening (Found : C, 64·1; H, 4·7. $C_8H_7O_2N$ requires C, 64·4; H, 4·7%). In acetone ($l = 1$, $c = 2·091$, $t = 20°$) :

λ	6708	6563	6162	5893	5461	5106
α	− 0·50°	− 0·56°	− 0·62°	− 0·70°	− 0·83°	− 0·91°
[α]	−24°	−27°	−30°	−33·5°	−40°	−43·5°

Action of Phenylhydrazine on (+)*Dioxindole.*—A mixture of (+)dioxindole (0·3 g.), phenylhydrazine (1 g.), and ethyl alcohol (6 c.c.) was refluxed for 6 hours. On cooling, yellow needles, m. p. 208°, separated. These were optically inactive in benzene, and the m. p. was not depressed

on admixture with isatin-β-phenylhydrazone (Fischer, *Ber.*, 1884, **17**, 577; Heller, *Ber.*, 1904, **37**, 938).

Action of Alcoholic Potash on (+)*Dioxindole.*—To an ethyl-alcoholic solution of (+)dioxindole ($l = 1$, $c = 1·964$) giving $\alpha_{5461} + 1·09°$, three drops of alcoholic potash ($0·5N$) were added. The optical activity vanished almost at once, and, when the solution was evaporated to dryness under diminished pressure, the residue, m. p. 245—246° (decomp.), was isatide. Under similar conditions, *r*-dioxindole and three drops of alcoholic potash ($0·8N$) gave isatide. *r*-Dioxindole, used alone, was recovered unchanged.

A gradual fall of rotation was, however, observed when an ethyl-alcoholic solution of (+)dioxindole was made less alkaline than above : thus, when three drops of alcoholic potash ($0·2N$) were added to a solution ($l = 1$, $c = 1·99$) giving $\alpha_{5461}^{20°} + 1·11°$, the following observations were made :

Time	2 (mins.)	3	7	12	22	37
$\alpha_{5461}^{20°}$	+0·95°	+0·80°	+0·77°	+0·72°	+0·64°	+0·58°
Time	47 (mins.)	62	1½ (hrs.)	2	20	24
$\alpha_{5461}^{20°}$	+0·53°	+0·48°	+0·42°	+0·38°	+0·24°	+0·24°

Acetylation of (+)*Dioxindole.*—Acetyl chloride (0·8 c.c.) was added gradually to (+)dioxindole (1 g.) at 0°, the colour changing to green and then to black. The mixture was kept at the ordinary temperature over-night and then triturated with water. The violet solid was recrystallised from water in presence of charcoal, colourless prisms, m. p. 130°, being obtained. In acetone these were optically inactive, and the m. p. was not depressed on admixture with authentic *r-O*-acetyldioxindole prepared by acetylating *r*-dioxindole with acetyl chloride.

Benzoylation of (+)*Dioxindole.*—Benzoyl chloride (2·2 c.c.) was added gradually at 0° to a solution of (+)dioxindole (1·2 g.) in pyridine. The product was crystallised from ethyl alcohol, needles (0·75 g.), m. p. 171—172°, and optically inactive in acetone, being obtained. The m. p. was not depressed on admixture with authentic *r*-dibenzoyldioxindole, prepared by benzoylating *r*-dioxindole either by the Schotten–Baumann method or by the action of benzoyl chloride in the presence of pyridine.

Action of Pyridine on (+)*Dioxindole.*—A solution of (+)dioxindole in pyridine which gave ($l = 1$, $c = 2·253$) $\alpha_{5461}^{16°} + 1·76°$, $[\alpha]_{5461}^{16°} + 78°$, gradually became optically inactive :

Hours	2½	20	44	93	188	331	433	501	551
$\alpha_{5461}^{16°}$	+1·66°	+1·43°	+1·20°	+0·80°	+0·44°	+0·13°	+0·04°	0·00°	0·00°

The optically inactive solution was evaporated to small bulk under diminished pressure and dilute sulphuric acid was added. A small amount of isatin was isolated.

Reduction of (+)*o-Nitromandelic Acid with Zinc Dust and Ammonium Hydroxide.*—Preliminary experiments on the reduction of *r-o*-nitromandelic acid with zinc dust and sulphuric acid on the lines adopted by Reissert (*Ber.*, 1908, **41**, 3921) for the preparation of *N*-hydroxyoxindole from *o*-nitrophenylacetic acid gave unsatisfactory yields of *N*-hydroxydioxindole. Reduction with zinc dust and ammonium hydroxide was more promising (Kalle and Co., D.R.-P. 184,693, 184,694, 189,841, 191,855; Heller, *Ber.*, 1909, **42**, 470), and this method was accordingly applied to (+)*o*-nitromandelic acid.

(+)*o*-Nitromandelic acid (5 g.) was dissolved in water (32 c.c.), 15 g. of aqueous ammonia (15%) and ammonium chloride (2·5 g.) added, and then zinc dust (5 g.) gradually with stirring (1 hour), the temperature being kept below 35°. The filtrate from the solid was acidified by hydrochloric acid (Congo-red). After several days under diminished pressure at the ordinary temperature (−)*N-hydroxydioxindole* [(−)*trioxindole*] (2 g.) separated; needles, m. p. 159° (decomp.), from light petroleum (b. p. 60—80°)–ethyl alcohol (Found : C, 58·4; H, 4·5. $C_8H_7O_3N$ requires C, 58·2; H, 4·3%). In acetone ($l = 1$, $c = 2·3$, $t = 20°$) :

λ	6708	6563	5893	5461	5106	4861	4358
α	− 0·88°	− 0·92°	− 1·15°	− 1·36°	− 1·52°	− 1·69°	− 2·05°
[α]	−38°	−40°	−50°	−59°	−66°	−73·5°	−89°

(+)*N-hydroxydioxindole*, prepared from (−)*o*-nitromandelic acid, forms prisms, m. p. 159° (decomp.), from water (Found : C, 58·1; H, 4·5. $C_8H_7O_3N$ requires C, 58·2; H, 4·3%). In acetone ($l = 1$, $c = 1·251$), $\alpha_{5461}^{20°} + 0·74°$, $[\alpha]_{5461}^{20°} + 59°$. The addition of a few drops of alcoholic potash to an ethyl-alcoholic solution of (+)*N*-hydroxydioxindole caused the deposition of the potassium derivative.

The optically active *N*-hydroxydioxindoles give a blue coloration with ferric chloride, and gradually reduce Fehling's solution at the ordinary temperature.

(−)o-*Hydroxymandelic Acid.*—A solution of sodium (−)o-aminomandelate (10·7 g.) in water (130 c.c.) was mixed with a solution of sodium nitrite (4 g.) in water (20 c.c.) and gradually added within 1 hour to 2N-sulphuric acid (115 c.c.) at 0°. The solution was heated until the evolution of nitrogen ceased, filtered from some resin, and extracted with ether, the ethereal solution dried, and the resulting oil (4·5 g.), which contained no nitrogen, kept for 9 days over calcium chloride under diminished pressure.

(−)o-*Hydroxymandelic acid* is a viscous oil which gives a blue coloration with ferric chloride (Found : C, 56·9; H, 5·0. $C_8H_8O_4$ requires C, 57·1; H, 4·8%). In acetone ($l = 2, c = 2·7285$), $\alpha_D^{20°} - 3·58°$, $[\alpha]_D^{20°} - 65·6°$; $\alpha_{5461}^{20°} - 4·18°$, $[\alpha]_{5461}^{20°} - 76·6°$. In ethyl ether ($l = 2, c = 2·7345$), $\alpha_D^{15°} - 2·94°$, $[\alpha]_D^{15°} - 53·8°$; $\alpha_{5461}^{15°} - 3·44°$, $[\alpha]_{5461}^{15°} - 62·9°$.

Similarly, *dl*-o-hydroxymandelic acid (6 g.) was prepared from sodium *r*-o-aminomandelate (13 g.) as a viscous oil. On reduction with hydriodic acid, it gave o-hydroxyphenylacetic acid, crystallising from water in needles, m. p. 141—141·5° (Found : C, 63·4; H, 5·4. Calc. for $C_8H_8O_3$: C, 63·1; H, 5·3%); Baeyer and Fritsch (*Ber.*, 1884, **17**, 973) give m. p. 137°, and Stoermer (*Annalen*, 1900, **313**, 83) m. p. 144—145°.

24.   *Arylamides of β-Arylaminocrotonic Acids.   Part II.*

By JOHN K. THOMSON and FORSYTH J. WILSON.

HAVING shown previously (J., 1933, 1262) that most of Jadhav's so-called β-arylamino-crotonoarylamides (*J. Indian Chem. Soc.*, 1930, **7**, 669) are the corresponding s-diarylureas, we have now prepared the real β-arylaminocrotonoarylamides; we have also found that the appearance and melting point of β-*p*-nitroanilinocrotono-*p*-nitroanilide as described by Jadhav are incorrect.

Arylamides of β-arylaminocrotonic acids should result from one molecule of ethyl acetoacetate and two molecules of arylamine : $CMe(OH){:}CH{\cdot}CO_2Et + 2RNH_2 = CMe(NHR){:}CH{\cdot}CO{\cdot}NHR + H_2O + EtOH$. Control of this reaction was difficult and the yields of β-arylaminocrotonoarylamides (diarylamides) were poor, intermediate and degradation products such as ethyl β-arylaminocrotonates, acetoacetarylamides, and diarylureas being usually obtained. As the acetoacetyl derivatives of the arylamines examined were easily accessible, the conditions governing the following reaction were investigated :
$COMe{\cdot}CH_2{\cdot}CO{\cdot}NHR \,[CMe(OH){:}CH{\cdot}CO{\cdot}NHR] + RNH_2 = CMe(NHR){:}CH{\cdot}CO{\cdot}NHR + H_2O$.
When the acetoacetarylamide and the corresponding arylamine were heated in an inert organic solvent under strictly neutral conditions, the reaction as judged by the appearance of water in the condensate proceeded, if at all, very slowly. The addition of a very small quantity of the arylamine hydrochloride, dilute hydrochloric acid, or iodine considerably shortened the time necessary to complete the reaction.

The above method (Method I) gave satisfactory yields in practically every case. In all cases, except with the nitroanilines, a method (Method II), which consisted in heating the β-aminocrotonoarylamide with the corresponding arylamine in an inert organic solvent, gave a slightly enhanced yield of crude product of better quality : $CMe(NH_2){:}CH{\cdot}CO{\cdot}NHR + RNH_2 = CMe(NHR){:}CH{\cdot}CO{\cdot}NHR + NH_3$.

In both methods the solvent should as far as possible fulfil the following conditions : (1) the boiling point should be as low as possible consistent with the rapid production of water or ammonia; if the temperature is too high, decomposition products make their appearance; (2) it should be immiscible with water; (3) at the boiling point a homogeneous mixture of the reactants should result and at the end of the reaction the diarylamide should separate on cooling.

All the β-arylaminocrotonoarylamides were easily hydrolysed by dilute hydrochloric acid in the cold (β-*p*-nitroanilinocrotono-*p*-nitroanilide requires to be heated to 30°) to

the corresponding acetoacetarylamides in yields between 80 and 90% of the theoretical, the loss being due to the slight solubility of the acetoacetarylamides in dilute hydrochloric acid.

EXPERIMENTAL.

The apparatus used for the preparation of β-arylaminocrotonoarylamides by Method I consisted of a 250 c.c. round-bottomed flask fitted with an inverted V-shaped air-condenser. The limb attached to the flask acted as a reflux condenser, the rate of heating being adjusted so that the condensing vapour just reached the bend in the condenser. The condensate from the free limb was collected in a small measuring cylinder; the water given off during the reaction, together with the water from the added aqueous acid, separated from the immiscible solvent on standing and gave an approximate measure of how far the reaction had proceeded. Heating was stopped when the distillate ceased to be turbid.

The apparatus used in Method II consisted of a 250 c.c. round-bottomed flask fitted with an ordinary air-condenser. Heating was continued till the evolution of ammonia ceased.

The β-aminocrotonoarylamides from *m*- and *p*-nitroaniline, *p*-anisidine, *o*- and *p*-chloroaniline were described by Jadhav (*loc. cit.*). These compounds and also the β-aminocrotonoarylamides from *p*-phenetidine, *p*-xylidine, *m*-4-xylidine, and *m*-chloroaniline have been prepared as follows : The acetoacetarylamide (20 g.) was ground to a paste with alcohol (50 c.c.), aqueous ammonia (50 c.c., *d* 0·88) added, and the solution filtered immediately from any impurity and unaltered acetoacetarylamide. On standing over-night (in a freezing mixture in the case of the *m*-chloroaniline derivative, which would otherwise tend to separate as an oil), the crystalline β-aminocrotonoarylamide was deposited; this was collected, thoroughly drained, pressed on porous tile, dried in a vacuum desiccator, and then recrystallised if necessary from warm alcohol to which some aqueous ammonia had been added. The alcoholic ammonia mother-liquors should not be concentrated, as slight decomposition may occur, but should be diluted with water and made just acid with hydrochloric acid with stirring and cooling. The amino-compound is thereby hydrolysed to the acetoacetarylamide, which is precipitated and can be collected and crystallised if necessary. The yield calculated on the acetoacetarylamide consumed in the reaction is almost theoretical. Estimations of the nitrogen in these compounds were carried out by the Dumas method, the carbon dioxide being generated externally and dried by sulphuric acid before entering the combustion tube, as otherwise low results due to hydrolysis of the amino-compound in the early stages of the estimation were obtained.

β-m-*Nitroanilinocrotono*-m-*nitroanilide*, CMe(NH·C₆H₄·NO₂)ːCH·CO·NH·C₆H₄·NO₂.—Acetoacet-*m*-nitroanilide (11·1 g.), *m*-nitroaniline (6·9 g.), toluene (70 c.c.), and 2N-hydrochloric acid (0·1 c.c.), Method I, 50 minutes. At the end of this time 40 c.c. of distillate were collected, from which 0·7 c.c. of water due to the reaction (theory, 0·9 c.c.) separated. The yellow mass deposited on cooling was boiled with 50 c.c. of absolute alcohol; the residue of β-m-*nitroanilinocrotono*-m-*nitroanilide* was washed with absolute alcohol and dried; further quantities were obtained by concentration of the toluene and alcohol mother-liquors. Yield, 79%.

β-Aminocrotono-*m*-nitroanilide (11·05 g.), *m*-nitroaniline (6·9 g.), and toluene (75 c.c.), Method II, 7 hours; the evolution of ammonia was slow. The substance (yield, 39%) crystallised from absolute alcohol in short yellow prisms, m. p. 152—153° (Found : C, 56·1; H, 4·2. $C_{16}H_{14}O_5N_4$ requires C, 56·1; H, 4·1%). Tars resulted when attempts were made to obtain this substance by Jadhav's method.

β-p-*Nitroanilinocrotono*-p-*nitroanilide*.—Acetoacet-*p*-nitroanilide (16·1 g.), *p*-nitroaniline (10 g.), *p*-nitroaniline hydrochloride (0·01 g.), and chlorobenzene (50 c.c.), Method I, 30 minutes. A red solid separated from the boiling mixture, and more on cooling; this was collected and treated with successive small quantities of warm alcohol till free from arylamine and mono-arylamide. The mother-liquor on concentration yielded a further small quantity of β-*p*-nitroanilinocrotono-*p*-nitroanilide. The product (yield, 94%), consisting of small, bright red prisms, m. p. 220—221°, was free from thermal decomposition products such as *s*-diarylurea. Yield, 94%. On crystallisation from a large quantity of 90% alcohol and drying at 60° a similar red material was obtained, which shrank considerably at about 200° and finally melted sharply at 221—222°; it was a *monohydrate* of β-p-*nitroanilinocrotono*-p-*nitroanilide* (Found : N, 15·6; loss at 115—120°, 5·3. $C_{16}H_{14}O_5N_4,H_2O$ requires N, 15·6; loss, 5·0%). There was no change in appearance on prolonged heating at 120°, neither was the melting point changed, though the shrinkage at 200° was rather less pronounced; heated at 140—150° in air, the compound decomposed completely (Found for substance dried at 115—120° : C, 55·6, 55·7; H, 4·1, 4·2; N, 16·3, 16·3. $C_{16}H_{14}O_5N_4$ requires C, 56·1; H, 4·1; N, 16·4%). Method II, β-aminocrotono-

p-nitroanilide (4·8 g.), *p*-nitroaniline (3·0 g.), chlorobenzene (50 c.c.), 10 hours. The evolution of ammonia was very slow and the quality of the product was inferior; yield, 70%. The quality and yield of the substance obtained by Jadhav's method were poor.

β-*p*-*Anisidinocrotono*-p-*anisidide*.—Method I, acetoacet-*p*-anisidide (10·35 g.), *p*-anisidine (6·15 g.), petroleum (b. p. 100—120°) (50 c.c.), and 2*N*-hydrochloric acid (0·1 c.c.), 1 hour; 0·6 c.c. of water (theory requires 0·9 c.c.) was given off in the reaction. The solvent was evaporated till the temperature of the mixture reached 125°; sufficient benzene was then added to give a homogeneous solution, from which colourless prisms separated on cooling, a further amount being obtained by concentration of the mother-liquors. The substance after recrystallisation from benzene melted at 116—117° (yield, 69%). The same substance was obtained in 83% yield by Method II, β-aminocrotono-*p*-anisidide (10·3 g.), *p*-anisidine (6·15 g.), petroleum (b. p. 100—120°) (50 c.c.), 4 hours, the solution being worked up as before [Found : (micro) C, 69·5; H, 6·5; N (macro), 9·1. $C_{18}H_{20}O_3N_2$ requires C, 69·2; H, 6·5; N, 9·0%].

β-*p*-*Aminocrotono*-p-*phenetidide* was prepared from acetoacet-p-*phenetidide* [plates, m. p. 104—105°. Found : N, 6·4. $C_{12}H_{15}O_3N$ requires N, 6·3%]. Limpach (*Ber.*, 1931, **64**, 970) does not give melting point or analysis] with alcohol and ammonia as already described; it formed rectangular plates, m. p. 123—124° (Found : N, 12·8. $C_{12}H_{16}O_2N_2$ requires N, 12·7%).

β-*p*-*Phenetidinocrotono*-p-*phenetidide* was prepared by Method I from acetoacet-*p*-phenetidide (11·05 g.), *p*-phenetidine (6·9 g.), petroleum (b. p. 100—120°) (50 c.c.), and 2*N*-hydrochloric acid (0·1 c.c.); 45 minutes. 0·8 C.c. (theory, 0·9 c.c.) of water was produced. Benzene was added to the warm reaction mixture; on cooling, colourless prisms, m. p. 105—106° after being washed with petroleum, were deposited (yield, 65%). It was also prepared by Method II, β-aminocrotono-*p*-phenetidide (11·0 g.), *p*-phenetidine (6·9 g.), petroleum (b. p. 100—120°) (50 c.c.), 90 minutes, the reaction mixture being worked up as before (yield, 96%). The m. p. of the crude washed substance was not altered by recrystallisation from absolute alcohol or benzene [Found : (micro) C, 70·3; H, 7·1; N (macro), 8·2. $C_{20}H_{24}O_3N_2$ requires C, 70·5; H, 7·1; N, 8·2%].

β-*Aminocrotono*-m-4-*xylidide*, prepared in the usual way from the acetoacet-*m*-4-xylidide, formed long colourless prisms, m. p. 124—125° (Found : N, 13·7. $C_{12}H_{16}ON_2$ requires N, 13·7%).

β-*m*-4-*Xylidinocrotono*-m-4-*xylidide* was prepared by Method I, from the acetoacet-*m*-xylidide (10·25 g.), *m*-xylidine (6·05 g.), petroleum (b. p. 100—120°) (50 c.c.), and 2*N*-hydrochloric acid (0·1 c.c.), 50 minutes; 0·85 c.c. of water (theory, 0·9 c.c.) was formed. On cooling, the substance was deposited as colourless prismatic needles (yield, 92%), m. p. 115—120° after being washed with petroleum and 126—127° after recrystallisation from absolute alcohol or benzene. The same substance was also obtained by Method II, β-aminocrotono-*m*-4-xylidide (10·2 g.), *m*-4-xylidine (6·05 g.), petroleum (b. p. 100—120°) (50 c.c.), 3 hours. A little benzene was added to the warm reaction mixture and the prismatic needles which separated (m. p. 118—120° after washing with petroleum) were purified as before, a further amount being obtained by concentrating the reaction mother-liquors [Found : (micro) C, 77·5; H, 8·0; N (macro), 9·1. $C_{20}H_{24}ON_2$ requires C, 77·8; H, 7·9; N, 9·1%].

β-*Aminocrotono*-p-*xylidide* was prepared in the usual way from acetoacet-p-*xylidide* [long prisms, m. p. 98—99°. Found : N, 7·0. $C_{12}H_{15}O_2N$ requires N, 6·8%]. Limpach (*loc. cit.*) does not give m. p. or analysis]; it formed long prisms, m. p. 136—137° (Found : N, 13·7. $C_{12}H_{16}ON_2$ requires N, 13·7%).

β-*p*-*Xylidinocrotono*-p-*xylidide* was obtained by Method I, acetoacet-*p*-xylidide (10·25 g.), *p*-xylidine (6·1 g.), petroleum (b. p. 100—120°) (50 c.c.), and 2*N*-hydrochloric acid (0·05 c.c.), 60 minutes; 0·85 c.c. of water (theory, 0·9 c.c.) was formed in the reaction. A further 50 c.c. of petroleum ether were added to the hot reaction mixture, which, on cooling, deposited long prisms; more was obtained on concentration. They melted at 106—108° after being washed with petroleum (yield, 89%) and 107—108° after recrystallisation from absolute alcohol. The same compound was obtained in 91% yield by Method II, β-aminocrotono-*p*-xylidide (10·2 g.), *p*-xylidine (6·1 g.), petroleum (b. p. 100—120°) (50 c.c.), 4 hours, the reaction mixture being worked up as before [Found : (micro) C, 77·8; H, 7·9; N (macro), 9·2. $C_{20}H_{24}ON_2$ requires C, 77·8; H, 7·9; N, 9·1%].

β-*o*-*Chloroanilinocrotono*-o-*chloroanilide* was prepared by Method I, acetoacet-*o*-chloroanilide (8·3 g.), *o*-chloroaniline (5·0 g.), petroleum (b. p. 100—120°) (50 c.c.), and 2*N*-hydrochloric acid (0·1 c.c.), 1 hour; 0·3 c.c. of water (theory, 0·7 c.c.) was formed. Varying the amount of acid and the time of heating had little effect on the yield of water. After almost complete evaporation of the solution the stiff oily residue was dissolved in dry ether and this solution was slowly

evaporated in a current of dry air. Large needles of the monoarylamide and large dense crystals of the desired substance separated; the latter crystals were picked out and again subjected to the same treatment with ether. The substance formed colourless, almost rectangular prisms with pyramidal ends, m. p. 99—100° (yield, 14%). The same substance was also obtained (yield, about 35%) by Method II, β-aminocrotono-*o*-chloroanilide (8·3 g.), *o*-chloroaniline (5·0 g.), petroleum (b. p. 100—120°) (50 c.c.), 6 hours, the reaction mixture being worked up as before [Found : (micro) C, 59·7; H, 4·6; N, 8·6; Cl, 22·2. $C_{16}H_{14}ON_2Cl_2$ requires C, 59·8; H, 4·4; N, 8·7; Cl, 22·1%]. The yields are poor owing to the laborious and wasteful method of purification. A solvent which will retain the acetoacetarylamide in solution while allowing the β-*o*-chloroanilinocrotono-*o*-chloroanilide to crystallise has not yet been found.

β-*Aminocrotono*-m-*chloroanilide* prepared from acetoacet-*m*-chloroanilide by the usual method, formed long prisms, m. p. 81—82° (Found : N, 13·1. $C_{10}H_{11}ON_2Cl$ requires N, 13·3%).

β-m-*Chloroanilinocrotono*-m-*chloroanilide* cannot be satisfactorily prepared by Method I, oils which are very difficult to solidify and work up being obtained. It was obtained by Method II, β-aminocrotono-*m*-chloroanilide (10·5 g.), *m*-chloroaniline (6·4 g.), petroleum (b. p. 100—120°) (50 c.c.), 90 minutes. On cooling, an oily layer separated; sufficient *iso*propyl ether (about 1 c.c.) to give a homogeneous solution at 25° was added and seed crystals of the substance were introduced. The solution on very slow cooling deposited a mass of small prisms, which was collected, washed with petroleum (b. p. 80—100°), and dried in a vacuum (yield, 51%). The seed crystals were obtained by keeping a solution of the oil in petroleum and ethyl ether at a low temperature for a prolonged time. The substance on recrystallisation first from a small quantity of *iso*propyl ether and then from a large quantity of petroleum (b. p. 80—100°) melted at 86—87° [Found : (micro) C, 60·0; H, 4·6; N (macro), 8·7. $C_{16}H_{14}ON_2Cl_2$ requires C, 59·8; H, 4·4; N, 8·7%].

β-p-*Chloroanilinocrotono*-p-*chloroanilide* was prepared by Method I, acetoacet-*p*-chloroanilide (8·3 g.), *p*-chloroaniline (5·0 g.), chlorobenzene (50 c.c.), and 2*N*-hydrochloric acid (0·15 c.c.), 40 minutes. The solution was then evaporated till the temperature of the residue reached 145°; the oily residue solidified when cooled and scratched. On crystallisation from benzene–petroleum (b. p. 100—120°), colourless prisms, m. p. 123—124°, were obtained (yield, 33%). The same compound was obtained in 43% yield by Method II, β-aminocrotono-*p*-chloroanilide (8·3 g.), *p*-chloroaniline (5·0 g.), petroleum (b. p. 100—120°) (50 c.c.), 5 hours. Benzene was added to the mixture after it had been slightly cooled; prisms of the substance separated on standing, and further amounts were obtained by addition of petroleum to the mixture [Found : (micro) C, 59·8; H, 4·5; N (macro), 8·7. $C_{16}H_{14}ON_2Cl_2$ requires C, 59·8; H, 4·4; N, 8·7%].

NOTES.

The Oxidation of 2- and 4-Nitro-4'-methyldiphenyl with Chromyl Chloride. By WILLIAM S. M. GRIEVE and DONALD H. HEY.

AN alternative method for the preparation of 4-nitrodiphenyl-4'-aldehyde has been sought in view of the irregularity of the m. p. (initially at 135°; 127° after repeated crystallisation from alcohol or benzene) of the material obtained by the nitration of diphenyl-4-aldehyde (J., 1933, 971).

4-*Nitrodiphenyl*-4'-*aldehyde.*—A suspension of 4-nitro-4'-methyldiphenyl (10 g.), prepared by the nitration of 4-methyldiphenyl (J., 1932, 1891), in redistilled carbon tetrachloride (350 c.c.) was gradually added to a stirred solution of chromyl chloride (18 g.) in carbon tetrachloride (40 c.c.) at room temperature (compare Law and Perkin, J., 1907, **91**, 258; 1908, **93**, 1633). After 2 days, the solution was poured into water and saturated with sulphur dioxide and the yellow solid was separated, washed with hot aqueous sodium bicarbonate, and recrystallised from alcohol, giving 4-nitrodiphenyl-4'-aldehyde (4·5 g.) in pale yellow needles, m. p. 127—128° alone or in admixture with the product obtained from the nitration of diphenyl-4-aldehyde (Found : C, 68·85; H, 4·0; N, 6·2. Calc. for $C_{13}H_9O_3N$: C, 68·7; H, 4·0; N, 6·2%). Acidification of the bicarbonate washings precipitated 4-nitrodiphenyl-4'-carboxylic acid (0·25 g., m. p. 330—335°; ethyl ester m. p. and mixed m. p. 112°). Evaporation of the clear dried

carbon tetrachloride layer left a crystalline yellow solid (5·0 g., m. p. 90—100°), which on re-peated crystallisation from light petroleum gave a further quantity of 4-nitrodiphenyl-4'-aldehyde and a small quantity of a second compound, m. p. 130—133°, which contained chlorine.

2-Nitrodiphenyl-4'-aldehyde.—A solution of 2-nitro-4'-methyldiphenyl (10 g.), prepared from sodium *p*-toluenediazoate and nitrobenzene (J., 1932, 1893), in carbon tetrachloride (50 c.c.), was similarly treated with chromyl chloride (15 g. in 50 c.c. of carbon tetrachloride). After the saturation with sulphur dioxide, evaporation of the dried carbon tetrachloride layer left a viscous residue, which was treated with saturated aqueous sodium bisulphite for 24 hours. The brown solid which separated was washed with ether and boiled with hydrochloric acid; the semi-solid residue, after several crystallisations from alcohol, yielded 2-nitrodiphenyl-4'-aldehyde (2 g.), m. p. 101° alone and in admixture with the product obtained in the nitration of diphenyl-4-aldehyde (Found : C, 69·1; H, 3·7; N, 6·6. Calc. for $C_{13}H_9O_3N$: C, 68·7; H, 4·0; N, 6·2%).—THE UNIVERSITY, MANCHESTER. [*Received, November 23rd, 1934.*]

Oxygen Addition Compounds of Acetylenes. By CHARLES A. YOUNG, R. R. VOGT, and J. A. NIEUWLAND.

IN order to explain the formation of the products of the reaction between acetylene and oxygen, Bodenstein (*Z. physikal. Chem.*, 1931, **12**, *B*, 155) postulated the intermediate formation of a peroxide.

We have found that many acetylenes upon exposure to oxygen or air liberate iodine from potassium iodide, oxidise ferrous to ferric compounds, form a yellow coloration with titanium sulphate, and give other reactions indicating the presence of active oxygen, probably in the form of peroxides. These oxygen derivatives will accordingly be referred to as peroxides in this paper.

A study of a wide variety of acetylenes, chiefly of the types RC⋮CH, RC⋮CR', and RC⋮CX, where R and R' represent alkyl and aryl groups, and X denotes a halogen, has shown that aromatic acetylenes acquire oxidising properties to a much less extent than do the alkyl deriv-atives. Only those acetylenes which are normally liquids or which have been melted appear to form peroxides. No peroxides have been found in acetylene itself. The behaviour of halogeno-acetylenes is somewhat irregular. Iodine linked to acetylenic carbon appears to retard the formation of peroxides in the lower members of the alkyl series, and in the higher members it apparently has little influence.

In several cases an acetylene was prepared by two or more widely different methods : all the samples formed peroxides with equal degrees of readiness and to the same extent. Con-sequently, it is improbable that the peroxides are due to traces of olefins present as impurities, since the same quantity of olefins would certainly not be formed by the various methods of preparation. It is possible that the acetylenes first polymerise, yielding olefinic derivatives which form peroxides. However, mono- and di-alkylacetylenes form similar quantities of peroxides. It is probable, therefore, that the acetylenes themselves form peroxides.

The peroxide of butylacetylene is rapidly destroyed by manganese dioxide, vanadium pentoxide, sodium peroxide, sodium hydroxide, metallic sodium, concentrated sulphuric acid, concentrated hydrochloric acid, silica gel, and bone black. Quinol greatly retards but does not prevent the formation of peroxides in butylacetylene. Traces of benzoyl peroxide or water accelerate for a few days the rate of peroxide formation in freshly distilled butylacetylene. Increased pressures of oxygen have no apparent effect.

During the past few years a number of cases have arisen in this laboratory in which rather anomalous results were obtained in polymerisation and other addition reactions of acetylenes. It is possible that these discrepancies in results were due to the catalytic action of the oxidising impurities in the acetylenes, and it is intended to repeat a number of these experiments with careful control of the peroxide impurities.—NOTRE DAME, INDIANA, U.S.A. [*Received, August 10th, 1934.*]

The Ferrohalides of Pyridine and Quinoline. By F. SHERWOOD TAYLOR.

THE elements manganese, cobalt, nickel, and copper form salts, R_2MHal_4(aq.) or $2RHal,MHal_2$ (aq.), where M is one of the above four metals, R is pyridinium or quinolinium, and Hal is chlorine or bromine. The colours of these salts, both in the solid state and in saturated aqueous solution, in general resemble those of solutions of the simple chloride, $MHal_2$, in the concentrated halogen acid. The colours of three of the four pyridinium and quinolinium ferrohalides now described follow the above rule.

Pyridinium Ferrochloride.—(1) Alcoholic solutions of pyridinium chloride and hydrated ferrous chloride were mixed : the yellow needles that separated were washed with acetone and dried in a current of dry carbon dioxide. (2) Hydrated ferrous chloride (20 g.) was mixed with concentrated hydrochloric acid (30 c.c.) and pyridine (16 g.). The solution was saturated with hydrogen sulphide, filtered, and reduced to half its bulk by distillation in a current of carbon dioxide. The yellow needles that separated were washed and dried as before; m. p. 127—128° after softening at about 110° [Found : (1) Fe, 15·6; Cl, 39·4; (2) Fe, 15·8; Cl, 39·8. $(C_5H_5NH)_2FeCl_4$ requires Fe, 15·6; Cl, 39·7%]. The *salt* was not deliquescent, but gradually darkened in air from pale yellow to orange. Concentrated aqueous solutions were yellow, but on dilution assumed the pale green colour associated with ferrous salts.

Quinolinium ferrochloride dihydrate, prepared by method (2) above, recrystallised from alcohol, washed with acetone, and dried in a current of carbon dioxide, formed small yellow leaflets [Found : Fe, 11·4; Cl, 28·7. $(C_9H_7NH)_2FeCl_4,2H_2O$ requires Fe, 11·6; Cl, 28·9%]. It softened at 86° and melted at 97° with some separation of solid. At higher temperatures water and quinolinium chloride were evolved.

Attempts to prepare the anhydrous material by mixing alcoholic solutions of the anhydrous constituents gave products which were apparently mixtures.

Pyridinium Ferrobromide.—A solution of " iron bromide " (25 g.) in hydrobromic acid (75 c.c., *d* 1·5) and water (30 c.c.) was saturated with hydrogen sulphide until the brown colour had disappeared. It was then sucked through a pad of asbestos fibre (to remove sulphur), pyridine (20 g.) added, and the solution distilled in a vacuum until crystals appeared on cooling. These were filtered off in an atmosphere of carbon dioxide and washed with acetone on the filter. The crystals were clear green when first washed, but on exposure to air darkened and deliquesced very rapidly and could not be dried without discoloration [Found : Fe, 10·4; Br, 58·9. $(C_5H_5NH)_2FeBr_4$ requires Fe, 10·4; Br, 59·7%]. The deliquescence, rapid oxidation, and green colour of this *salt* are in marked contrast to the properties of the other salts here described.

Quinolinium ferrobromide dihydrate was prepared by essentially the same method as was used for pyridinium ferrobromide. The mixed solutions, however, after concentration in a vacuum, set solid, and this solid was recrystallised from hot acetone. The crystals were filtered off, washed with cold acetone, and dried in a current of dry carbon dioxide. They were bright yellow with a tinge of orange [Found : Fe, 8·4; Br, 47·5. $(C_9H_7NH)FeBr_4,2H_2O$ requires Fe, 8·3; Br, 47·6%]. When heated, they darkened, softened at 81°, and melted at 89° with some separation of solid.—East London College, University of London. [*Received, October 22nd,* 1934.]

Action of Nitric Acid upon p-*Hydroxyphenyltrimethylammonium Iodide.* By KENNETH C. ROBERTS.

IN an attempt to synthesise 2-amino-4-dimethylaminophenol it was observed that dilute nitric acid reacts with *p*-hydroxyphenyltrimethylammonium iodide (I) in the manner indicated (I⟶II), 3-nitration being accompanied by replacement of I' by NO_3' and nuclear iodination. Both the *iodonitro-nitrate* (II) and the corresponding *iodide* (III) resisted decomposition to the tertiary base.
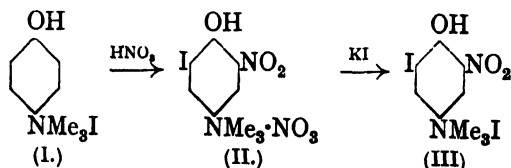
5(?)-*Iodo-3-nitro-4-hydroxyphenyltrimethylammonium Nitrate* (II).—Treatment of (I) with 2*N*-nitric acid at the boiling point gave a red solution which decomposed violently with evolution of iodine. The mixture was boiled until no free iodine remained; the solid obtained crystallised from water in yellow needles, decomp. above 210° (Found : C, 27·8; H, 4·0. $C_9H_{13}O_6N_2I$ requires C, 28·0; H, 3·1%).
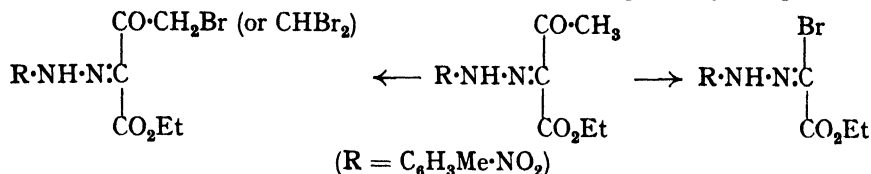
5(?)-*Iodo-3-nitro-4-hydroxyphenyltrimethylammonium Iodide* (III).—An aqueous solution of (II) with potassium iodide (cf. *Ber.*, 1919, **52**, 295) gave a dark yellow, crystalline precipitate. After recrystallisation from water this decomposed above 225° (Found : N, 6·4, 6·5. $C_9H_{12}O_3N_2I_2$ requires N, 6·2%).—KING'S COLLEGE, LONDON. [*Received, November 22nd,* 1934.]

25. *The 3-Carbethoxy-4-hydroxy-1-nitrotolylpyrazoles.*

F. D. Chattaway, D. R. Ashworth, and M. Grimwade.

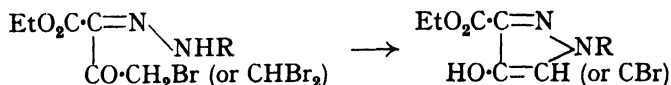The nitrotolyldiazonium salts couple readily with ethyl acetoacetate to give the nitrotolylazoacetoacetates.

Bromine acts upon these compounds in the same way as upon other arylazoacetoacetates (cf. J., 1933, 475), and either replaces the acetyl group as a whole, when action takes place in acetic acid containing sodium acetate, or substitutes in the acetyl group when boiling acetic acid or chloroform is the solvent, ethyl α-bromoglyoxylate-nitrotolylhydrazones or ethyl nitrotolylazo-γ-bromo- or -$\gamma\gamma$-dibromo-acetoacetates respectively being formed :

$$R\cdot NH\cdot N\overset{\displaystyle CO\cdot CH_2Br \text{ (or } CHBr_2)}{\underset{\displaystyle CO_2Et}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}} \quad \longleftarrow \quad R\cdot NH\cdot N\overset{\displaystyle CO\cdot CH_3}{\underset{\displaystyle CO_2Et}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}} \quad \longrightarrow \quad R\cdot NH\cdot N\overset{\displaystyle Br}{\underset{\displaystyle CO_2Et}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}$$
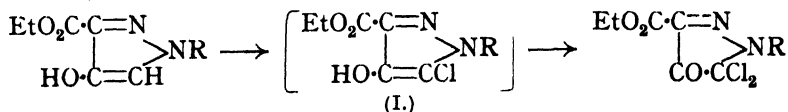
$$(R = C_6H_3Me\cdot NO_2)$$

Only with ethyl 6-nitro-*o*-tolylazoacetoacetate dissolved in acetic acid containing sodium acetate does bromine, even when excess is used, substitute in the nucleus, the halogen, when this occurs, entering the para-position, ethyl α-bromoglyoxylate-4-bromo-6-nitro-*o*-tolylhydrazone being formed.

Compounds containing bromine in the nucleus can readily be obtained by coupling the appropriate brominated nitrotolyldiazonium salt with ethyl acetoacetate, and subsequent action of bromine upon these coupled products.

The bromine atoms which have either replaced or substituted the acetyl group are very reactive. For instance, on treatment with alcoholic ammonia, the ethyl α-bromoglyoxylate-nitrotolylhydrazones yield the corresponding α-amino-compounds. Also, on heating with alcoholic potassium acetate, the γ-bromoacetoacetates lose hydrogen bromide, with ring closure and formation of the corresponding 4-hydroxypyrazoles, whilst the $\gamma\gamma$-dibromoacetoacetates similarly yield 5-bromo-4-hydroxypyrazoles, identical with those obtained by the action of bromine upon the corresponding 4-hydroxypyrazoles obtained as above :

$$\underset{CO\cdot CH_2Br \text{ (or } CHBr_2)}{\overset{EtO_2C\cdot C=N}{\underset{|}{\overset{|}{}}}}\!\!\!\!\!\Big\rangle NHR \quad \longrightarrow \quad \underset{HO\cdot C=CH \text{ (or } CBr)}{\overset{EtO_2C\cdot C=N}{\underset{|}{\overset{|}{}}}}\!\!\!\!\!\Big\rangle NR$$
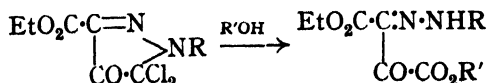
When chlorine is passed into a chloroform solution of any one of the 3-carbethoxy-4-hydroxy-1-nitrotolylpyrazoles, two atoms of chlorine substitute in the 5-position of the pyrazole ring, and 5 : 5-dichloro-3-carbethoxy-1-nitrotolyl-4-pyrazolones are formed (cf. J., 1933, 1389) :

$$\underset{HO\cdot C=CH}{\overset{EtO_2C\cdot C=N}{\underset{|}{\overset{|}{}}}}\!\!\!\Big\rangle NR \longrightarrow \left[\underset{HO\cdot C=CCl}{\overset{EtO_2C\cdot C=N}{\underset{|}{\overset{|}{}}}}\!\!\!\Big\rangle NR\right] \longrightarrow \underset{CO\cdot CCl_2}{\overset{EtO_2C\cdot C=N}{\underset{|}{\overset{|}{}}}}\!\!\!\Big\rangle NR$$

<div align="center">(I.)</div>

In the case of the 4-hydroxy-mono- and -di-brominated nitrotolylpyrazoles the presence of halogen in the tolyl nucleus checks the action, which does not proceed beyond the first stage, the corresponding 5-chloro-4-hydroxy-pyrazole (I) being the final product.

The 5 : 5-dichloro-1-nitrotolyl-4-pyrazolones are rather unstable, viscous solids of so low a melting point that in some cases they could not be obtained crystalline. They are all reduced by hydriodic acid to the corresponding 5-chloro-pyrazoles (I).

When the 5 : 5-dichloro-4-pyrazolones are heated with alcohols, the pyrazole ring is opened and esters of diketosuccinic acid nitrotolylhydrazone are formed :

$$\underset{CO\cdot CCl_2}{\overset{EtO_2C\cdot C=N}{\underset{|}{\overset{|}{}}}}\!\!\!\Big\rangle NR \xrightarrow{R'OH} \underset{CO\cdot CO_2R'}{\overset{EtO_2C\cdot C:N\cdot NHR}{\underset{|}{\overset{|}{}}}}$$

EXPERIMENTAL.

*Ethyl 2-Nitro-*p-*tolylazoacetoacetate.*—A solution of 20 g. of 2-nitro-*p*-toluidine in the minimum quantity of acetic acid was poured into 100 c.c. of concentrated hydrochloric acid, the suspension diazotised at 0° with 10 g. of sodium nitrite in 30 c.c. of water, and the resulting filtered diazonium solution added dropwise to a mixture of 140 g. of crystalline sodium acetate, 20 g. of ethyl acetoacetate, and 100 c.c. of 50% aqueous alcohol. The above *compound* separated at once and was collected after 12 hours. It crystallised from alcohol in yellow prisms, m. p. 142°. Yield, 90% of the theoretical (Found : N, 14·5. $C_{13}H_{15}O_5N_3$ requires N, 14·3%).

Similarly were prepared the following ethyl acetoacetates (all were crystallised from alcohol) : 3-*nitro*-p-*tolylazo*, pale yellow needles, m. p. 104° (Found : N, 14·5%); 5-*nitro*-o-*tolylazo*, pale yellow prisms, m. p. 128° (Found : N, 14·4%); 4-*nitro*-o-*tolylazo*, yellow prisms, m. p. 131° (Found : N, 14·5%); 6-*bromo*-2-*nitro*-p-*tolylazo*, yellow prisms, m. p. 92° (Found : Br, 21·6. $C_{13}H_{14}O_5N_3Br$ requires Br, 21·5%); 6-*nitro*-o-*tolylazo*, yellow rhombic plates, m. p. 81° (Found : N, 14·3%); 6-*bromo*-3-*nitro*-p-*tolylazo*, pale yellow prisms, m. p. 126° (Found : Br, 21·6%); 4-*bromo*-5-*nitro*-o-*tolylazo*, yellow prisms, m. p. 182° (Found : Br, 21·4%); 4-*bromo*-6-*nitro*-o-*tolylazo*, yellow rhombic plates, m. p. 84° (Found : Br, 21·5%); 6-*bromo*-4-*nitro*-o-*tolylazo*, yellow, long, slender prisms, m. p. 131° (Found : Br, 21·7%); 2 : 6-*dibromo*-3-*nitro*-p-*tolylazo*, pale yellow, rhombic plates, m. p. 102° (Found : Br, 35·4. $C_{13}H_{13}O_5N_3Br_2$ requires Br, 35·5%); 4 : 6-*dibromo*-5-*nitro*-o-*tolylazo*, yellow prisms, m. p. 146° (Found : Br, 35·7%).

*Ethyl α-Bromoglyoxylate-2-nitro-*p-*tolylhydrazone.*—3 G. of bromine in 5 c.c. of acetic acid were added to a solution of 5 g. of ethyl 2-nitro-*p*-tolylazoacetoacetate and 2 g. of crystalline sodium acetate in 15 c.c. of cold acetic acid. The mixture became warm and, on cooling, the above *compound* separated. It crystallised from alcohol in yellow prisms, m. p. 160° (Found : Br, 24·1. $C_{11}H_{11}O_4N_3Br$ requires Br, 24·2%). In a similar manner the following ethyl α-bromo-glyoxylate-hydrazones were obtained (all were crystallised from alcohol) : 3-*nitro*-p-*tolyl*, pale yellow needles, m. p. 142° (Found : Br, 24·0%); 5-*nitro*-o-*tolyl*, pale yellow prisms, m. p. 150° (Found : Br, 24·4%); 6-*nitro*-o-*tolyl*, orange-yellow prisms, m. p. 132° (Found : Br, 24·4%); 6-*bromo*-2-*nitro*-p-*tolyl*, orange-yellow flattened prisms, m. p. 99° (Found : Br, 38·9. $C_{11}H_{11}O_4N_3Br_2$ requires Br, 39·1%); 6-*bromo*-3-*nitro*-p-*tolyl*, pale yellow prisms, m. p. 153° (Found : Br, 39·0%); 4-*bromo*-5-*nitro*-o-*tolyl*, yellow prisms, m. p. 164° (Found : Br, 39·3%); 4-*bromo*-6-*nitro*-o-*tolyl* (by the action of 1 mol. of bromine upon ethyl 4-bromo-6-nitro-*o*-tolylazoacetoacetate in cold acetic acid and by the action of an excess of bromine upon ethyl 6-nitro-*o*-tolylazoacetoacetate in hot acetic acid), orange prisms, m. p. 127° (Found : Br, 39·3%); 2 : 6-*dibromo*-3-*nitro*-p-*tolyl*, very pale yellow, rectangular plates, m. p. 99° (Found : Br, 50·1. $C_{11}H_{10}O_4N_3Br_3$ requires Br, 50·3%); 4 : 6-*dibromo*-5-*nitro*-o-*tolyl*, pale yellow prisms, m. p. 116° (Found : Br, 50·3%).

*Ethyl α-aminoglyoxylate-5-nitro-*o-*tolylhydrazone*, prepared by stirring the corresponding α-bromo-compound into alcohol saturated with ammonia gas, crystallised from alcohol in orange prisms, m. p. 152° (Found : N, 20·9. $C_{11}H_{14}O_4N_4$ requires N, 21·05%).

Similarly were obtained : *ethyl α-aminoglyoxylate-4-bromo-5-nitro-*o-*tolylhydrazone*, red prisms from alcohol, m. p. 174° (Found : Br, 23·4. $C_{11}H_{13}O_4N_4Br$ requires Br, 23·2%); *ethyl α-aminoglyoxylate-4 : 6-dibromo-5-nitro-*o-*tolylhydrazone*, yellow prisms from alcohol, m. p. 160° (Found : Br, 37·8. $C_{11}H_{12}O_4N_4Br_2$ requires Br, 37·7%).

*Ethyl 2-Nitro-*p-*tolylazo-γ-bromoacetoacetate.*—1·6 G. of bromine in 5 c.c. of acetic acid were added to 3 g. of ethyl 2-nitro-*p*-tolylazoacetoacetate in 10 c.c. of boiling glacial acetic acid. On cooling, the above *compound* separated as a yellow solid. It crystallised from alcohol in small yellow needles, m. p. 139° (Found : Br, 21·3. $C_{13}H_{14}O_5N_3Br$ requires Br, 21·5%).

Similarly were prepared the following ethyl γ-bromoacetoacetates, all of which were crystallised from alcohol : 3-*nitro*-p-*tolylazo*, yellow prisms, m. p. 113° (Found : Br, 21·7%); 5-*nitro*-o-*tolylazo*, yellow prisms, m. p. 136° (Found : Br, 21·6%); 6-*nitro*-o-*tolylazo* (with chloroform instead of acetic acid as solvent), yellow rhombic plates, m. p. 117° (Found : Br, 21·4%); 4-*nitro*-o-*tolylazo*, which separated from solution in alcohol as a labile form in long, yellow, hair-like prisms which gradually redissolved while the stable form separated as yellow rectangular plates, m. p. 145° (Found : Br, 21·6%); 6-*bromo*-2-*nitro*-p-*tolylazo*, yellow prisms, m. p. 121° (Found : Br, 35·4. $C_{13}H_{13}O_5N_3Br_2$ requires Br, 35·5%); 6-*bromo*-3-*nitro*-p-*tolylazo*, small yellow prisms, m. p. 137° (Found : Br, 35·6%); 4-*bromo*-5-*nitro*-o-*tolylazo*, yellow prisms, m. p. 144° (Found : Br, 35·3%); 4-*bromo*-6-*nitro*-o-*tolylazo*, yellow prisms, m. p. 122° (Found : Br, 35·5%); 6-*bromo*-4-*nitro*-o-*tolylazo*, long, slender, yellow prisms, m. p. 157° (Found : Br, 35·7%); 2 : 6-*dibromo*-3-*nitro*-p-*tolylazo*, pale yellow, rhombic plates, m. p. 133° (Found : Br,

45·4. $C_{12}H_{11}O_5N_3Br_2$ requires Br, 45·3%); 4 : 6-*dibromo*-5-*nitro*-o-*tolylazo*, yellow prisms, m. p. 139° (Found : Br, 45·1%).

Ethyl 2-Nitro-p-*tolylazo-γγ-dibromoacetoacetate.*—3·2 G. of bromine in 5 c.c. of acetic acid were added to 3 g. of ethyl 2-nitro-*p*-tolylazoacetoacetate in 10 c.c. of boiling acetic acid. On cooling, the above *compound* separated; it crystallised from alcohol in yellow, long, slender prisms, m. p. 141° (Found : Br, 35·3. $C_{12}H_{11}O_5N_3Br_2$ requires Br, 35·5%).

In a similar manner the following ethyl γγ-dibromoacetoacetates were prepared (crystallised from alcohol) : 3-*nitro*-p-*tolylazo*, small yellow prisms, m. p. 143° (Found : Br, 35·6%); 5-*nitro*-o-*tolylazo*, pale yellow prisms, m. p. 170° (Found : Br, 35·4%); 6-*nitro*-o-*tolylazo* (with chloroform instead of acetic acid as solvent), yellow rhombic plates, m. p. 88° (Found : Br, 35·3%); 6-*bromo*-2-*nitro*-p-*tolylazo*, yellow prisms, m. p. 156° (Found : Br, 45·3. $C_{12}H_{10}O_5N_3Br_3$ requires Br, 45·3%); 6-*bromo*-3-*nitro*-p-*tolylazo*, yellow, long, slender prisms, m. p. 157° (Found : Br, 45·4%); 4-*bromo*-5-*nitro*-o-*tolylazo*, yellow prisms, m. p. 161° (Found : Br, 45·1%); 4-*bromo*-6-*nitro*-o-*tolylazo*, yellow prisms, m. p. 104° (Found : Br, 45·3%); 2 : 6-*dibromo*-3-*nitro*-p-*tolylazo*, pale yellow prisms, m. p. 130° (Found : Br, 52·7. $C_{12}H_{11}O_5N_3Br_4$ requires Br, 52·5%); 4 : 6-*dibromo*-5-*nitro*-o-*tolylazo*, yellow prisms, m. p. 163° (Found : Br, 52·5%).

*Formation of 3-Carbethoxy-4-hydroxy-1-(2'-nitro-*p-*tolyl)pyrazole.*—3 G. of potassium acetate were added to a solution of 5 g. of ethyl 2-nitro-*p*-tolylazo-γ-bromoacetoacetate in 50 c.c. of boiling alcohol. A vigorous action took place and the solution darkened, potassium bromide separating. After cooling, on careful addition of water to the resulting solution, the above *compound* separated as a dark solid. It crystallised from alcohol in yellow, long, slender prisms, m. p. 119° (Found : N, 14·6. $C_{13}H_{13}O_5N_3$ requires N, 14·4%).

Similarly were obtained the following 3-carbethoxy-4-hydroxy-1-tolylpyrazoles, all of which were crystallised from alcohol : 3'-*nitro*-p-*tolyl*, colourless, short, flattened prisms, m. p. 182° (Found : N, 14·2%); 5'-*nitro*-o-*tolyl*, pale yellow prisms, m. p. 114° (Found : N, 14·5%); 6'-*nitro*-o-*tolyl*, pale yellow, short, flattened prisms, m. p. 99° (Found : N, 14·2%); 4'-*nitro*-o-*tolyl*, colourless hair-like needles, m. p. 177° (Found : N, 14·3%); 4'-*bromo*-6'-*nitro*-o-*tolyl*, colourless rhombic plates, m. p. 162° (Found : Br, 21·8. $C_{13}H_{12}O_5N_3Br$ requires Br, 21·6%); 6'-*bromo*-4'-*nitro*-o-*tolyl*, colourless, short, flattened prisms, m. p. 183° (Found : Br, 21·8%); 6'-*bromo*-2'-*nitro*-p-*tolyl*, very pale yellow, rhombic plates, m. p. 165° (Found : Br, 21·4%); 2' : 6'-*dibromo*-3'-*nitro*-p-*tolyl*, colourless, short, flattened prisms, m. p. 184° (Found : Br, 35·7. $C_{13}H_{11}O_5N_3Br_2$ requires Br, 35·6%); 4' : 6'-*dibromo*-5'-*nitro*-o-*tolyl*, colourless, long, slender prisms, m. p. 219° (Found : Br, 35·9%). The *acetyl* derivative of the last compound (warm acetic anhydride and a drop of sulphuric acid) crystallised from alcohol in colourless, long, slender prisms, m. p. 196° (Found : Br, 32·3. $C_{15}H_{13}O_6N_3Br_2$ requires Br, 32·6%).

*5-Bromo-3-carbethoxy-4-hydroxy-1-(5'-nitro-*o-*tolyl)pyrazole.*—(I) 1·5 G. of potassium acetate were added to a solution of 3 g. of ethyl 5-nitro-*o*-tolylazo-γγ-dibromoacetoacetate in 25 c.c. of boiling alcohol. A vigorous action took place and the solution darkened. On cooling and careful addition of water the above *compound* separated as a yellow solid. It crystallised from alcohol in colourless compact prisms, m. p. 133° (Found : Br, 21·8. $C_{13}H_{12}O_5N_3Br$ requires Br, 21·6%).

(II) 2 G. of bromine in 2 c.c. of acetic acid were added to a solution of 3 g. of 3-carbethoxy-4-hydroxy-1-(5'-nitro-*o*-tolyl)pyrazole in 10 c.c. of boiling acetic acid. On careful addition of water to the resulting solution a yellow solid was obtained which on crystallisation was found to be identical with the above 5-bromo-pyrazole.

Similarly have been prepared : 5-*bromo*-3-*carbethoxy*-4-*hydroxy*-1-(3'-*nitro*-p-*tolyl)pyrazole*, colourless, long, slender prisms from alcohol, m. p. 143° (Found : Br, 21·5%); 5-*bromo*-3-*carbethoxy*-4-*hydroxy*-1-(6'-*nitro*-o-*tolyl)pyrazole*, colourless, short, flattened prisms from alcohol, m. p. 146° (Found : Br, 21·7%).

*Formation of 5 : 5-Dichloro-3-carbethoxy-*1-*(4'-nitro-*o-*tolyl)-*4-*pyrazolone.*—1·5 G. of 3-carbethoxy-4-hydroxy-1-(4'-nitro-*o*-tolyl)pyrazole were dissolved in 10 c.c. of chloroform, and chlorine passed for 10 minutes. On removal of the chloroform on a water-bath the above *compound* remained as a viscous oil, which solidified on standing and scratching with ether. It crystallised from chloroform and light petroleum in yellow, long, slender prisms, m. p. 124° (Found : Cl, 20·0. $C_{13}H_{11}O_5N_3Cl_2$ requires Cl, 19·7%).

The 2'-nitro-*p*-tolyl, 5'-nitro-*o*-tolyl, 6'-nitro-*o*-tolyl, and 3'-nitro-*p*-tolyl analogues were similarly obtained as viscous oils, which could not be made to crystallise but yielded crystalline derivatives.

*Formation of 5-Chloro-3-carbethoxy-4-hydroxy-*1-*(4'-nitro-*o-*tolyl)pyrazole.*—2 G. of potassium iodide in 5 c.c. of water were added to 2 g. of 5 : 5-dichloro-3-carbethoxy-1-(4'-nitro-*o*-tolyl)-4-

pyrazolone dissolved in 25 c.c. of acetic acid at 60°. After 20 minutes, sodium sulphite solution was added dropwise until all the iodine was removed. Subsequent careful addition of water precipitated the above *compound*. It crystallised from alcohol in clusters of colourless, long, slender prisms, m. p. 181° (Found : Cl, 10·7. $C_{12}H_{13}O_5N_3Cl$ requires Cl, 10·9%).

The following analogues were similarly prepared : 5'-*nitro-o-tolyl*, stellate clusters of colourless, long, slender prisms, m. p. 101° (Found : Cl, 10·8%); 6'-*nitro-o-tolyl*, pale yellow, flattened, rectangular prisms, m. p. 135° (Found : Cl, 11·1%); 3'-*nitro-p-tolyl*, colourless, irregular, compact plates, m. p. 128° (Found : Cl, 10·6%).

Formation of 1-*Ethyl* 2-*Methyl Diketosuccinate-*1-(4'-*nitro-o-tolyl*)*hydrazone.*—2 G. of 5 : 5-dichloro-3-carbethoxy-1-(4'-nitro-*o*-tolyl)-4-pyrazolone were heated for 2 minutes in 10 c.c. of methyl alcohol. On cooling, the above *compound* separated as a viscous solid. It crystallised from ethyl alcohol in yellow, long, slender prisms, m. p. 145° (Found : N, 12·6. $C_{16}H_{19}O_7N_3$ requires N, 12·5%).

Similarly, by using the appropriate alcohol, were obtained the 5'-*nitro-o-tolyl* analogue, yellow hair-like needles from methyl alcohol, m. p. 139° (Found : N, 12·5%), and the 2'-*nitro-p-tolyl* analogue, yellow slender prisms from alcohol, m. p. 132° (Found : N, 12·4%), and *diethyl diketosuccinate-*2-*nitro-*p-*tolylhydrazone*, yellow, long, slender needles from alcohol, m. p. 97° (Found : N, 11·9. $C_{15}H_{17}O_7N_3$ requires N, 12·0%).

Formation of 5-*Chloro-*3-*carbethoxy-*4-*hydroxy-*1-(6'-*bromo-*2'-*nitro-*p-*tolyl*)*pyrazole.*—2 G. of 3-carbethoxy-4-hydroxy-1-(6'-bromo-2'-nitro-*p*-tolyl)pyrazole were dissolved in 10 c.c. of chloroform, and chlorine passed for 10 minutes. On removal of the chloroform the above *compound* remained as a viscous solid. It crystallised from alcohol in colourless, irregular, flattened prisms, m. p. 168° (Found : Cl, 8·7; Br, 19·6. $C_{13}H_{11}O_5N_3ClBr$ requires Cl, 8·8; Br, 19·8%).

The following were similarly obtained, and crystallised from alcohol : 6'-*bromo-*4'-*nitro-o-tolyl*, colourless compact prisms, m. p. 202° (Found : Cl, 8·9; Br, 19·9%); 4'-*bromo-*6'-*nitro-o-tolyl*, yellow, short, compact prisms, m. p. 164° (Found : Cl, 8·8; Br, 19·9%); 2' : 6'-*dibromo-*3'-*nitro-o-tolyl*, colourless, short, rectangular prisms with domed ends, m. p. 169° (Found : Cl, 7·4; Br, 33·1. $C_{13}H_{10}O_5N_3ClBr_2$ requires Cl, 7·4; Br, 33·1%); 4' : 6'-*dibromo-*5'-*nitro-o-tolyl*, colourless, compact, flattened, rectangular prisms, m. p. 165° (Found : Cl, 7·3; Br, 32·9%).

THE QUEEN'S COLLEGE LABORATORY, OXFORD.   [*Received, October* 15*th,* 1934.]

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26. *The Constituents of Guaiacum Resin. Part III. Synthesis of dl-*Guaiaretic Acid Diethyl Ether.
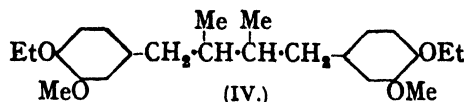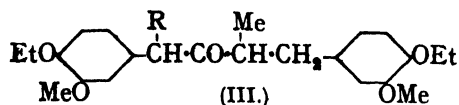
By ROBERT D. HAWORTH and THOMAS RICHARDSON.

THE synthesis of guaiaretic acid dimethyl ether (J., 1934, 1423) confirmed the main features of the formula (I; R = H) first suggested for guaiaretic acid by Schroeter, Lichtenstadt, and Irineu (*Ber.*, 1918, **51**, 1587), but the positions of the ethylenic linkage and the phenolic hydroxyl groups remained undetermined. Although the optical activity of guaiaretic acid can be explained by either formula (I; R = H) or (II), the latter fails to account for the facile transformation of the acid into derivatives of 1-phenylnaphthalene. Further, (II) can be discarded, as it has now been shown that neither formaldehyde nor formic acid is obtained by ozonisation of *l*-guaiaretic acid dimethyl ether in chloroform solution. The remaining problem, concerning the position of the two phenolic hydroxyl groups, has now been settled in favour of formula (I; R = H) by an unambiguous synthesis of guaiaretic acid diethyl ether (I; R = Et).
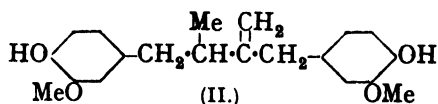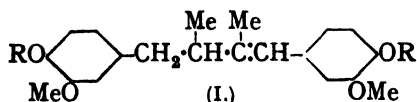
β-3-*Methoxy-*4-*ethoxyphenyl-*α-*methylcrotonic acid*, prepared from 3-methoxy-4-ethoxy-benzaldehyde and ethyl α-bromopropionate, was reduced to β-3-*methoxy-*4-*ethoxyphenyl-*α-*methylpropionic acid*. The methyl ester of this acid and 3-*methoxy-*4-*ethoxyphenylaceto-nitrile*, obtained by the action of acetic anhydride on the oxime of 3-methoxy-4-ethoxy-phenylpyruvic acid (Barger, Eisenbrand, Eisenbrand, and Schittler, *Ber.*, 1933, **66**, 453),

condensed in the presence of potassium ethoxide to give an oily cyano-ketone, which was hydrolysed with concentrated hydrochloric acid in cold acetic acid solution to β-*keto-αδ-bis-(3-methoxy-4-ethoxyphenyl)-γ-methylvaleramide* (III; R = CO·NH$_2$). This amide was

EtO⟨⟩(MeO)–CH·CO·CH·CH$_2$⟨⟩(OMe)–OEt   (R, Me above) (III.)

EtO⟨⟩(MeO)–CH$_2$·CH·CH·CH$_2$⟨⟩(OMe)–OEt   (Me Me above) (IV.)

converted by alkaline hydrolysis into αδ-*bis-(3-methoxy-4-ethoxyphenyl)-γ-methylbutan-β-one* (III; R = H), which, in contrast to the corresponding tetramethoxy-ketone described in the previous memoir (*loc. cit.*, p. 1428), was readily obtained in the crystalline condition. The ketone (III; R = H) reacted with methylmagnesium iodide, yielding a carbinol, which was dehydrated with potassium hydrogen sulphate to dl-*guaiaretic acid diethyl ether*, m. p. 103—104° (I; R = Et). Catalytic reduction afforded optically inactive *dihydroguaiaretic acid diethyl ether*, m. p. 98—99° (IV). *l*-Guaiaretic acid, obtained from guaiacum resin as described by Schroeter, Lichtenstadt, and Irineu (*loc. cit.*), was ethylated to give l-*guaiaretic acid diethyl ether*, which was reduced catalytically to an optically inactive dihydro-derivative, m. p. 98—99°, identical with the synthetic product (IV) mentioned above. The identity was also confirmed by the preparation of the *dibromo-* and the *dinitro*-derivatives.

EXPERIMENTAL.

3-*Methoxy-4-ethoxyphenylacetonitrile.*—A solution of 3-methoxy-4-ethoxyphenylpyruvic acid (40 g.) and hydroxylamine hydrochloride (15 g.) in 8% sodium hydroxide solution (250 c.c.) was heated at 100° for 1·5 hours. Acidification of the cold solution precipitated the oxime (35 g.), which was dried and heated with acetic anhydride (140 g.) at 100° for 2 hours. The anhydride was removed under reduced pressure and the residue was dissolved in ether, washed with sodium bicarbonate solution, dried, recovered, and distilled. The *nitrile*, b. p. 156—158°/0·4 mm., crystallised from methyl alcohol in pale yellow prisms (18 g.), m. p. 53—54° (Found : C, 69·3; H, 6·7. C$_{11}$H$_{13}$O$_2$N requires C, 69·1; H, 6·9%).

β-3-*Methoxy-4-ethoxyphenyl-α-methylcrotonic Acid.*—A solution of 3-methoxy-4-ethoxy-benzaldehyde (40 g.) in benzene (120 c.c.) was heated on the water-bath with zinc filings (17 g.) and ethyl α-bromopropionate (56 g.). After the initial violent reaction had subsided, the heating was continued for ¼ hour. The mixture was decomposed with dilute sulphuric acid and the product, isolated with benzene, was heated with potassium hydrogen sulphate (20 g.) at 180° for ¼ hour. The *ethyl* ester was extracted with ether and distilled; it boiled at 195—200°/15 mm., and crystallised from benzene–light petroleum in stout prisms, m. p. 58—60° (Found : C, 67·9; H, 7·8. C$_{15}$H$_{20}$O$_4$ requires C, 68·2; H, 7·6%). Hydrolysis with methyl-alcoholic potassium hydroxide yielded the *acid*, which crystallised from benzene in colourless needles (28 g.), m. p. 127—128° (Found : C, 66·0; H, 6·8. C$_{13}$H$_{16}$O$_4$ requires C, 66·1; H, 6·8%).

β-3-*Methoxy-4-ethoxyphenyl-α-methylpropionic acid*, obtained in 80% yield by reduction of the above crotonic acid with sodium amalgam, crystallised from ether–light petroleum in colourless plates, m. p. 63—64° (Found : equiv., 240. C$_{13}$H$_{18}$O$_4$ requires equiv., 238). The methyl ester, prepared by the Fischer–Speier method, was a colourless oil, b. p. 158—160°/0·3 mm.

β-*Keto-αδ-bis-(3-methoxy-4-ethoxyphenyl))-γ-methylvaleramide* (III; R = CO·NH$_2$).—A solution of methyl β-(3-methoxy-4-ethoxyphenyl)-α-methylpropionate (8·6 g.) and 3-methoxy-4-ethoxyphenylacetonitrile (6 g.) in benzene (120 c.c.) was added to a suspension of potassium ethoxide (prepared from 2·1 g. of potassium) in benzene (20 c.c.). After heating on the water-bath for 6 hours, the cyano-ketone was extracted with 1% sodium hydroxide solution, recovered, and isolated with ether as an oil, which did not crystallise and gave a transient purple colour with ferric chloride. The crude cyano-ketone (7·2 g.), dissolved in a mixture of glacial acetic acid (10 c.c.) and concentrated hydrochloric acid (30 c.c.), was saturated with hydrogen chloride at 0° and kept for 3 days. The mixture was diluted with water and extracted with ether; the extract was washed several times with water and then with dilute sodium bicarbonate solution, dried, and the solvent removed. The residual *amide* (III; R = CO·NH$_2$) solidified on cooling and crystallised from benzene–light petroleum in colourless plates (3·3 g.), m. p. 114—115° (Found : C, 67·1; H, 7·2. C$_{24}$H$_{31}$O$_5$N requires C, 67·1; H, 7·3%). The amide was soluble in sodium hydroxide solution and gave a violet colour with ferric chloride.

αδ-*Bis-(3-methoxy-4-ethoxyphenyl)-α-methylbutan-β-one* (III; R = H).—The above amide

(6 g.) was boiled with 20% sodium hydroxide solution (35 c.c.) for 4 hours. The alkali-insoluble product, isolated with ether, boiled at 230—235°/0·3 mm., and crystallised from ether–light petroleum in colourless prisms (1·5 g.), m. p. 57—58° (Found : C, 71·3; H, 8·0. $C_{23}H_{26}O_5$ requires C, 71·5; H, 7·8%). The *dinitro*-derivative crystallised from acetic acid in cream needles, m. p. 133—134° (Found : C, 58·2; H, 5·7. $C_{23}H_{24}O_9N_2$ requires C, 58·0; H, 5·9%), and reduction with zinc dust and hydrochloric acid yielded an amine which gave a blue colour with ferric chloride.

d1-*Guaiaretic Acid Diethyl Ether* (I; R = Et).—A solution of methylmagnesium iodide (from 0·3 g. of magnesium and 0·8 c.c. of methyl iodide) in ether (15 c.c.) was gradually added to an ice-cold solution of the above ketone (III; R = H) (1 g.) in ether (15 c.c.). After 1 hour, the mixture was heated on the water-bath for ¼ hour, and decomposed with ammonium chloride solution. The carbinol (0·9 g.), isolated with ether, was heated with potassium hydrogen sulphate (1 g.) at 150° for 1 hour. The product was extracted with ether and washed first with water and then with dilute sodium hydroxide solution; removal of the solvent gave an oil, which rapidly solidified and then crystallised from methyl alcohol in colourless prisms (0·35 g.), m. p. 103—104° (Found : C, 74·8; H, 8·4. $C_{24}H_{32}O_4$ requires C, 75·0; H, 8·4%).

l-*Guaiaretic Acid Diethyl Ether* (I; R = Et).—Ethyl iodide (4 g.) was gradually added to a boiling suspension of the potassium salt, obtained by adding a solution of potassium hydroxide (1·2 g.) in 80% alcohol (16 c.c.) to l-guaiaretic acid (1·5 g.) in alcohol (5 c.c.). After 3 hours, the alcohol was removed, the residue diluted with water, and the solid (1·7 g.) collected. Three crystallisations from methyl alcohol yielded the *diethyl* ether (1·1 g.) as colourless prisms, m. p. 95—96°; $[\alpha]_D^{19°} - 48\cdot0°$ in ethyl alcohol (c = 0·835) (Found : C, 74·7; H, 8·5. $C_{24}H_{32}O_4$ requires C, 75·0; H, 8·4%).

Optically Inactive Dihydroguaiaretic Acid Diethyl Ether (IV).—A rapid stream of hydrogen was passed for 3 hours through a boiling alcoholic solution (15 c.c.) of either l- or d1-guaiaretic acid diethyl ether (1 g.) in presence of palladised charcoal (1·0 g. of 0·5%). The liquid was filtered and evaporated, leaving a residue, which crystallised from methyl alcohol in colourless prisms, m. p. 98—99° (Found : C, 74·7; H, 8·4. $C_{24}H_{34}O_4$ requires C, 74·6; H, 8·9%). No depression in m. p. was observed when specimens prepared from the two sources were mixed. The compound was optically inactive in alcohol or chloroform solution. The *dibromo*-derivative, obtained by the action of bromine (2 mols.) in acetic acid solution, crystallised from acetic acid in colourless needles, m. p. 134—135° (Found : Br, 29·5. $C_{24}H_{32}O_4Br_2$ requires Br, 29·4%). The *dinitro*-derivative, prepared by the action of concentrated nitric acid (2 mols.) in acetic acid solution, crystallised from acetic acid in cream-coloured prisms, m. p. 111—112° (Found : C, 60·5; H, 6·8. $C_{24}H_{32}O_8N_2$ requires C, 60·8; H, 6·7%).

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27. *The Veratrine Alkaloids.   Parts I and II.*

By B. K. BLOUNT.

Part I.   The Constitution of Veratridine.

IT is more than fifty years since Wright and Luff (J., 1878, **33**, 341) described the separation of commercial veratrine into cevadine, veratridine ($C_{37}H_{53}O_{11}N$), and cevadilline. These authors ascribed to cevadine the constitution of an ester of tiglic acid with a base cevine, $C_{27}H_{43}O_8N$. This has since been fully confirmed, and cevine, originally obtained only in an amorphous condition, has since been crystallised (Freund and Schwarz, *Ber.*, 1899, **32**, 800). For veratridine, Wright and Luff proposed the constitution of an ester of veratric acid with " verine," which was supposed to have the composition $C_{26}H_{45}O_8N$; and this proposal has not since been challenged. The fact, however, that pure cevine is obtained in excellent yield by the hydrolysis of crude veratrine (containing therefore veratridine) (Macbeth and Robinson, J., 1922, **121**, 1574) must give rise to the suspicion that Wright and Luff's amorphous verine is really slightly impure cevine. This matter has now been examined.

Both veratridine and cevadine could be obtained in a pure condition by Wright and

Luff's method, but the process proved tedious and wasteful, and a better method, which gives a 21% yield of veratridine, is described in the experimental section. Veratridine is amorphous, but can be purified by crystallisation of the hydrated acid sulphate described by Wright and Luff. The base is optically active, having $[\alpha]_D^{22°} + 8.0°$ in alcohol.

On hydrolysis, veratridine gave veratric acid and a crystalline base, which proved to be identical with cevine. Veratridine is therefore veratroylcevine, and must have the composition $C_{36}H_{51}O_{11}N$.

<center>EXPERIMENTAL.</center>

Isolation of Veratridine from Commercial Veratrine.—To a solution of commercial veratrine (10 g.) in $N/10$-sulphuric acid (150 c.c.), sodium nitrate (40 c.c. of 20%) was added drop by drop with constant stirring. A sparingly soluble nitrate separated in an amorphous but easily filtrable condition, and was collected and washed with dilute sodium nitrate solution. The base was regenerated from the nitrate, washed, and dissolved (wet) in $2N$-sulphuric acid (10 c.c.). To this solution, saturated aqueous ammonium sulphate was added drop by drop in amount just insufficient to cause a permanent turbidity. On standing, or immediately on seeding, veratridine sulphate separated in long, thin, silky needles. After being kept for some hours at 0°, the sulphate was collected and washed with a little ammonium sulphate solution. The free base was regenerated, and dried in a vacuum (1·9 g.). The filtrate from the sulphate was again precipitated with sodium nitrate, and the purification through the sulphate repeated, whereby a further 0·2 g. of veratridine was obtained, bringing the total yield up to 2·1 g.

For further purification the crude veratridine was reconverted into the *sulphate*, which was recrystallised several times. It formed a mass of white silky needles, which on drying in the air coalesced to a hard brittle resin. For analysis the substance was drained on a porous plate in an atmosphere saturated with water vapour (Found : C, 46·5; H, 7·6. $C_{36}H_{51}O_{11}N,H_2SO_4,9H_2O$ requires C, 46·3; H, 7·6%). On drying (high vac. at 110°), the substance lost sulphuric acid as well as water, and the product was very hygroscopic (Found : C, 59·3; H, 7·7; loss, 22·6. $C_{36}H_{51}O_{11}N,\frac{1}{2}H_2SO_4$ requires C, 59·8; H, 7·2; loss, 21·9%).

The free base, regenerated from the pure sulphate, formed a colourless amorphous powder, almost completely insoluble in water (wherein it differs from amorphous cevadine, which is appreciably soluble), and having $[\alpha]_D^{22°} + 8.0°$ (4% solution in 96% alcohol). When heated, it softened and melted over the range 160—180°. It retained water tenaciously. After drying for some days in an evacuated desiccator, and then for 15 hours at 0·001 mm. over phosphoric oxide, it was by no means anhydrous (Found : C, 61·7; H, 7·8; N, 2·2. $C_{36}H_{51}O_{11}N,1·5H_2O$ requires C, 61·7; H, 7·8; N, 2·2%). On drying at 110° in a high vacuum, the substance lost its adsorbed water, but also decomposed slightly with further loss of water (Found : C, 65·5; H, 7·7; loss, 5·6. $C_{36}H_{51}O_{11}N$ requires C, 64·2; H, 7·6; loss, 3·9%. $C_{36}H_{51}O_{11}N$, having lost an additional 0·7 molecule of water, requires C, 65·5; H, 7·6; loss, 5·7%).* The colour reactions of veratridine are : (1) Concentrated hydrochloric acid; colourless, changing during a few days to pale orange-pink. (2) Concentrated sulphuric acid; orange-red, with *no* fluorescence; after 24 hours, becoming crimson and acquiring a blue fluorescence. (3) Mixed with sugar, and moistened with sulphuric acid : intense green, becoming blue, and finally dirty purple. (4) Mixed with phosphoric oxide and kept in a loosely stoppered tube : a pink colour develops after some hours. The corresponding reactions of cevadine are : (1) Colourless, remaining so (*not* violet, as is stated in the literature). (2) Bright yellow, with an intense green fluorescence. The colour rapidly changes to orange, then more slowly to crimson-red, and the fluorescence changes to greenish-blue. (3) Similar to veratridine, but not so intense. (4) Similar to veratridine.

The filtrate from the insoluble nitrate was treated with ammonia, and the precipitate collected, dried, and dissolved in alcohol (7 c.c.). Cevadine crystallised readily on seeding, and was collected after 24 hours. Yield, 0·9 g. of a white crystalline powder, m. p. 199—201°. It was pure after a single recrystallisation.

The various mother-liquors are being examined for subsidiary alkaloids.

Hydrolysis of Veratridine.—Veratridine (2 g.) in alcohol (3 c.c.) was mixed with a solution of potassium hydroxide (4 g.) in the same solvent (10 c.c.), and the mixture refluxed for $\frac{1}{2}$ hour.

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* The author is not suggesting the existence of a definite hydrate. His object is simply to show that the analytical figures are in complete agreement with the formula proposed, provided that allowance is made for adsorbed water, which is lost on drying together with a little constitutional water. Such behaviour is not unusual among complex amorphous compounds.

On cooling, the characteristic potassium derivative of cevine separated; it was washed with cold saturated alcoholic caustic potash and then with ether, dissolved in water (10 c.c.), and decomposed with carbon dioxide; the white crystalline solid (1·15 g.) obtained was identified as cevine by its m. p. and mixed m. p., its crystal form and solubilities, and by the m. p. and mixed m. p. of its methiodide (Freund and Schwarz, *J. pr. Chem.*, 1917, **96**, 238).

The aqueous filtrate from the cevine was made acid with concentrated hydrochloric acid, giving a copious white precipitate, which was collected. A further small amount was obtained by diluting the alcoholic mother-liquors from the potassium cevine and making them acid, followed by extraction with ether, shaking with aqueous sodium carbonate, and precipitation with acid. The combined crops of acid were crystallised from water, giving pure veratric acid, m. p. 179°. The yield (0·49 g.) was not much below that theoretically possible (0·54 g.).

Part II. Cevine.

Cevadine (Freund and Schwarz, *Ber.*, 1899, **32**, 800) and veratridine, the two main constituents of commercial veratrine, can both be hydrolysed to give a crystalline base, cevine, $C_{27}H_{43}O_8N$, about which little is known. It is a tertiary base, and of the eight oxygen atoms two are present as hydroxyl groups, two are contained in a lactone group, and the function of the remaining four is uncertain. On distillation with soda-lime it gives a small amount of a volatile base, almost certainly *l*-coniine.

All attempts to investigate the structure of cevine by a study of its oxidation (see particularly Macbeth and Robinson, *J.*, 1922, **121**, 1574) have been unsuccessful. The molecule either breaks down completely or gives amorphous products. It is necessary, therefore, to find a new method of attack which, while preserving the greater part of the carbon skeleton, will nevertheless give crystalline products. Dehydrogenation with selenium, which has hitherto been applied to only one other alkaloid, yohimbine (Mendlik and Wibaut, *Rec. trav. chim.*, 1931, **50**, 91; Barger and Scholz, *Helv. Chim. Acta*, 1933, **16**, 1343), has proved to be such a method.

As the result of a number of comparative experiments, conditions have been found which give a crystalline base in a yield (as crude picrate) of nearly 10%. This base, termed *cevanthridine*, appears to have the composition $C_{23}H_{25}N$, and this formula is supported by the analyses of the *hydrochloride* and *methiodide*. The properties of cevanthridine suggest that it contains a phenanthridine nucleus, and mention should be made of its similarity in many respects to the base thebenidine, obtained by the zinc-dust distillation of thebenine (Vongerichten, *Ber.*, 1901, **34**, 768). The formula of cevanthridine corresponds to that of thebenine, $C_{15}H_9N$, with the addition of C_8H_{16}, *i.e.*, saturated side chains.

At higher temperatures the yield of cevanthridine is diminished and a crystalline hydrocarbon can be isolated. As yet it has been isolated only in very small amount.

Work on the further degradation of cevanthridine is in progress.

Experimental.

Cevanthridine.—Hydrated cevine (5 g.) and selenium (10 g.), contained in a 25 c.c. Pyrex flask provided with a short air-condenser, were heated together by means of a metal bath. The temperature of the bath was kept at 270—280° for ¼ hour, then gradually raised during the next ¼ hour to 320—330°, and kept at this temperature for 15 hours. The water which was given off in the earlier stages was driven over from time to time by warming the air condenser. This was necessary to avoid splashing of the hot melt due to refluxing of drops of water. After cooling, the flask was broken and the regulus separated, powdered, and extracted continuously for 12 hours with ether. The extract was orange in colour, later deepening to brown, and had an intense green fluorescence. The ethereal extract was shaken with dilute sulphuric acid, which caused the separation of dark-coloured resinous salts, from which the ethereal solution * was decanted. The insoluble salts were washed with ether, and the bases liberated and taken up in ether. After drying over potassium carbonate, the ether was removed, the gummy residue dissolved in acetone (5 c.c.), and picric acid (2 g.) in acetone (5 c.c.) added. On scratching or seeding, an orange-brown crystalline picrate separated, which, after cooling at 0° for some hours, was collected and washed with acetone and ether. Yield, about 0·4 g.

Attempts to purify the picrate were not successful. Even after five recrystallisations from acetone, correct analytical figures were not obtained (Found : C, 65·2; H, 5·3; N, 9·5%).

The following method of purification was finally adopted. The picrate was decomposed, and the base crystallised from acetone, collected, dissolved in boiling alcohol (10 c.c.), and treated with hot 2N-sulphuric acid (10 c.c.). On cooling, the sparingly soluble yellow sulphate separated. The base regenerated from this was crystallised from acetone (charcoal). After two further crystallisations from the same solvent pure *cevanthridine* was obtained as colourless plates, m. p. 207° (Found : C, 87·8, 87·5, 87·7; H, 8·0, 7·7, 8·1; N, 4·4, 4·6, 4·7. $C_{23}H_{25}N$ requires C, 87·6; H, 8·0; N, 4·4%). The yield from 5 g. of cevine amounted to about 100 mg.

Cevanthridine dissolves in neutral organic solvents to give colourless solutions with a marked violet fluorescence. Its salts with hydrochloric, nitric, and sulphuric acids are very sparingly soluble in water, are yellow in colour, and in solution show an intense green fluorescence. The *hydrochloride*, prepared from the base (20 mg.) in boiling alcohol (1 c.c.) by the addition of 2N-hydrochloric acid (0·5 c.c.), formed long, thin, lemon-yellow needles, which sintered and darkened above 230°, and were finally molten at 245° (Found : C, 72·7; H, 7·7. $C_{23}H_{25}N,HCl,1·5H_2O$ requires C, 72·9; H, 7·7%).

The *picrate*, prepared from the base (15 mg.) in boiling acetone (4 c.c.) and picric acid (12 mg.) in acetone (1 c.c.), crystallised on cooling in bright yellow prisms, which blackened and decomposed at 230—240°. Analysis showed that the substance, although apparently homogeneous, contained picric acid in rather less than the 1 : 1 ratio (Found : C, 65·1, 65·2; H, 5·4, 5·4; N, 8·8%. Cf. analysis of the picrate in the previous section).

When cevanthridine (20 mg.) and methyl iodide (1 c.c.) were warmed together, the base dissolved at once, the solution rapidly became yellow, and the *methiodide* soon separated in rosettes of microscopic yellow plates. After refluxing for 1½ hours, the mixture was cooled, and the product collected and washed with ether (Found : C, 62·8; H, 6·1; I, 27·8. $C_{24}H_{28}NI$ requires C, 63·0; H, 6·2; I, 27·8%). The substance melts at 254—256° (decomp.), sintering and darkening a few degrees lower, and is very sparingly soluble in most solvents. When its suspension in hot alcohol is treated with a drop of aqueous potash, an intense green colour is produced. This rapidly fades, leaving a pale purple-red solution in which black particles are suspended.

The Crystalline Hydrocarbon.—The ethereal solution (marked * above) on evaporation gave a resinous residue, which in some cases deposited traces of crystalline material. If the dehydrogenation is carried out at a higher temperature (360° for 20 hours), the yield of crude cevanthridine picrate is diminished (0·08 g.) and the amount of non-basic crystalline material increases. The non-basic fraction from such a dehydrogenation was treated in ethereal solution with charcoal, the filtrate evaporated, and the residue crystallised from methyl alcohol (2 c.c.). The crude crystallisate was dried and sublimed in a high vacuum. At 0·001 mm. sublimation was rapid at 130°. The sublimate was again crystallised from methyl alcohol (0·7 c.c.), giving rosettes of very thin, colourless needles, m. p. 139—143° with previous sintering. Though the substance was obviously still impure, the yield (2·5 mg.) did not allow of further purification (Found : C, 90·3; H, 8·0%). The *hydrocarbon* dissolves in concentrated sulphuric acid to an orange solution having a yellowish-green fluorescence. This solution slowly becomes green and then blue. The picrate forms long red needles, readily soluble in most solvents.

28. *Relative Oxidation Potentials of Nitric Acid Solutions.*

By R. G. MONK and H. J. T. ELLINGHAM.

MEASUREMENTS of the *E.M.F.* of cells of the type $Pt|HNO_3$ solution│standard reference electrode, for nitric acid concentrations up to about 15M were made by Ihle (*Z. physikal. Chem.*, 1896, **19**, 577), and single potentials of the electrode system, $Pt|HNO_3$ solution, derived from his results (neglecting liquid-junction potential) have been quoted as representing the relative oxidising tendencies of nitric acid solutions of different concentrations. As Ihle showed qualitatively, however, these potentials are notably affected by additions of nitrite, and since no attempt was made to control or estimate the con-

centration of nitrous acid or other reducing substances in the various nitric acid solutions used, the observed " oxidation potentials " must have been affected to unknown and pro-bably varied extents by traces of such substances which happened to be present in these solutions.

In later work on this type of electrode system, the concentration of reducing substances has been controlled by supplying nitric oxide to the electrode so as to establish the equilibrium $HNO_3 + 2NO + H_2O \rightleftharpoons 3HNO_2$ (Abegg and Pick, *Z. anorg. Chem.*, 1906, **51**, 1; Moore, *J. Amer. Chem. Soc.*, 1913, **35**, 333; Klemenc and Hayek, *Z. anorg. Chem.*, 1930, **186**, 181; Bode, *ibid.*, 1931, **195**, 201). Such potential measurements have been confined, however, to concentrations up to about M-nitric acid; so also have investigations of this equilibrium by other methods (Lewis and Edgar, *J. Amer. Chem. Soc.*, 1911, **33**, 292; Abel and Schmid, *Z. physikal. Chem.*, 1928, **136**, 430). At higher concentrations, complic-ations arise through the increasing importance of other equilibria, such as $NO + 2HNO_3 \rightleftharpoons 3NO_2 + H_2O$, which has been studied recently by Abel, Schmid, and Stein (*Z. Elektrochem.*, 1930, **36**, 692).

On the other hand, it is at higher concentrations that the oxidising properties of nitric acid become particularly strongly developed, and, owing to the importance of such solutions as oxidising systems, it seems very desirable to attempt to obtain at least some relative measure of their oxidising tendency. The present investigation has been undertaken with this object.

From the work of Ihle (*loc. cit.*) and from observations on the cathodic reduction of nitric acid solutions (Ellingham, *J.*, 1932, 1565), there is good reason to believe that the electrode equilibrium

$$HNO_3 + 2H^{\cdot} + 2\ominus \rightleftharpoons HNO_2 + H_2O \quad . \quad . \quad . \quad . \quad . \quad (1)$$
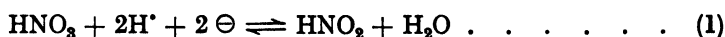
is readily established at an indifferent electrode in moderately concentrated nitric acid solutions containing nitrous acid, and that it may be the principal equilibrium controlling the electrode potential over wide ranges of concentration. If this is true, the single potential of such an electrode system with a specified nitric acid concentration at 25° will be given by :

$$e = e_0' - 0 \cdot 0296 \log [HNO_2] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $[HNO_2]$ is the activity of nitrous acid in the solution, and e_0' a constant *for the given nitric acid concentration*, provided that the concentration of nitrous acid be kept sufficiently small compared with that of nitric acid, so that the activities of nitric acid and the hydrogen ion can be regarded as constant. For the general case where the nitric acid concentration is also varied,

$$e = e_0 + 0 \cdot 0296 \log [HNO_3][H^{\cdot}]^2/[HNO_2][H_2O] \quad . \quad . \quad . \quad (3)$$

where symbols in square brackets represent the activities of the corresponding substances in solution, and e_0 is a general constant—the standard electrode potential corresponding to the equilibrium (1). Owing to lack of information as to activities, especially of that of the hydrogen ion, in more concentrated nitric acid solutions, it is not possible to determine e_0 from values of e for solutions of known nitric acid and nitrous acid concentration by (3). If it be assumed, however, that the molar concentration of nitrous acid is a satisfactory measure of $[HNO_2]$ in nitric acid solutions containing very small proportions of nitrous acid, measurements of e for such solutions enable values of e_0' for various nitric acid concentra-tions to be calculated by (2). Values of e_0' obtained in this way should afford a relative measure of the oxidising tendency of nitric acid solutions of various concentrations.

Measurements have been made, therefore, of the *E.M.F.* of the cell

$$Pt \,|\, HNO_3, HNO_2 \text{ solution} \,\vdots\, \text{satd. } KNO_3 \,\vdots\, N\text{-}KCl, Hg_2Cl_2 \,|\, Hg,$$

using nitric acid solutions of several different concentrations to which various small amounts of sodium nitrite had been added, the actual concentration of nitrous acid at equilibrium being determined analytically. The *E.M.F.* of this cell is taken as a measure of the single potential, e, of the electrode system, $Pt \,|\, HNO_3, HNO_2$ solution, with reference to the normal calomel electrode, and all values of e quoted below have this significance. Strictly, the

values of the *E.M.F.* should be corrected for liquid-junction potential in order to obtain *e*, since the use of saturated potassium nitrate solution as intermediate liquid is not likely to eliminate this factor completely, especially at higher nitric acid concentrations. There is, however, no means of determining the magnitude of the residual liquid-junction potential for these solutions, and uncorrected *E.M.F.* data have therefore been used throughout.

EXPERIMENTAL.

Solutions of accurately known nitric acid concentration (ranging from M to about $12M$) and of various approximately known nitrous acid concentrations (up to about $0.3M$) were prepared by running ice-cold sodium nitrite solution under a cooled nitric acid solution. The amount of nitric acid used (in the form of a standard solution) was that calculated to give the desired concentration of this acid when the solution was made up to a standard volume at 25°, due allowance having been made for that converted into sodium nitrate by reaction with the nitrite. After complete mixing had occurred, the solution was transferred to a thermostat and made up to the standard volume (50 c.c.) when its temperature had risen to 25°.

The sodium nitrite had been recrystallised from aqueous solution and dried over sulphuric acid in a vacuum. The nitric acid had been twice redistilled (once over potassium and silver nitrates).

Solutions prepared in this way were introduced into the electrode vessel, which consisted of a glass tube fitted with a ground-glass stopper through which was sealed a thin platinum wire. Welded to the end of this wire, so as to hang freely in the solution, was the electrode of stout platinum wire, the lower part of which was coiled into the form of a flat spiral. After each measurement, the electrode was washed, left for a short time in distilled water, and then heated to whiteness in the blowpipe flame. A bent capillary tube sealed to the bottom of the electrode vessel led to an intermediate vessel containing saturated potassium nitrate solution. The siphon tube of a normal calomel electrode dipped into a second intermediate vessel containing saturated potassium nitrate which communicated with the first by way of an H-tube, one limb of which was plugged with filter-paper.

The cell was set up in a thermostat at 25°, and its *E.M.F.* measured at intervals until constancy was attained. The time required for this decreases with increasing concentrations of both nitric and nitrous acids. In the more dilute nitric acid solutions, the effect of nitrous acid in catalysing the establishment of equilibrium (Ihle, *loc. cit.*) is very marked, and, if the nitrous acid concentration is also low, several hours may be required for the *E.M.F.* to become constant. In such cases, values of *e* were plotted against time in order to be able to follow the approach to equilibrium conditions. In the most dilute nitric acid solution employed ($1.045M$) the results became unreliable owing to uncertainty as to the establishment of true equilibrium. In the more concentrated solutions values of *e* were reproducible to about 1 millivolt.

Determination of Nitrous Acid by Means of Lead Peroxide.—The determination of small amounts of nitrous acid in relatively concentrated nitric acid solutions presents some difficulty, since standard analytical methods become inaccurate or inapplicable under these conditions. A method suitable for the present purpose was devised, however, by utilising the reaction $PbO_2 + HNO_3 + HNO_2 = Pb(NO_3)_2 + H_2O$. Lead peroxide was purified by boiling with 10% sodium hydroxide solution and then with dilute nitric acid. After being washed free from nitrate by distilled water, it was preserved under dilute nitric acid. Before use, the peroxide was filtered off and again washed in order to ensure removal of any traces of nitrate.

For the determination, excess of the wet peroxide was introduced into a conical flask and shaken into a suspension with a little water. The nitrous acid solution, diluted if necessary so that its nitric acid concentration was less than $6M$, was run in and kept for 10 minutes with occasional shaking. The residual peroxide was then filtered off on a sintered-glass filter and washed thoroughly with distilled water. The lead in the filtrate and washings was determined gravimetrically as sulphate.

In order to test the reproducibility of the method, samples of approximately $6M$-nitric acid to which various small amounts of nitrite had been added were kept for 2 hours with occasional shaking, and 25 c.c. portions of each sample were then allowed to react with the peroxide under the above conditions. For one such sample the weights of lead sulphate obtained from the several portions were respectively 0.0634, 0.0631, 0.0638, and 0.0631 g.; giving a nitrous acid concentration of 0.0083_5 M with a probable error of about 0.5%. Over the range of nitrous acid concentration used, the probable error of the determination estimated in this way is of the order of 1%. Blank determinations on nitric acid solutions (up to $6M$)

which had been freed as far as possible from nitrous acid gave up to 0·8 mg. of lead sulphate per 25 c.c., which corresponds to 0·0001M-nitrous acid. Since, according to relation (2) above, an error as great as 8% in the nitrous acid concentration represents an error of only 1 millivolt in the electrode potential, the accuracy of the analytical method is adequate for the present purpose.

Results.—The observed values of e are shown plotted against log c_{HNO_2} in the accompanying figure, where c_{HNO_2} denotes concentration of nitrous acid in g.-mol. per litre. Each line on this diagram refers to the concentration of nitric acid specified below it. In each case the line is drawn with the theoretical slope of 0·0296, and in the position which best represents the points corresponding with the lower concentrations of nitrous acid.

It will be seen that, for values of log c_{HNO_2} between $\bar{3}$·5 and about $\bar{1}$·0, the values of e for each concentration of nitric acid vary closely in accordance with the relation

$$e = e_0' - 0.0296 \log c_{HNO_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

Values of e_0' obtained by extrapolation of the lines are as follows :

HNO$_3$, g.-mols. per l.	11·88	8·60	6·08	4·13	2·21	1·045
e_0', volt	0·824	0·772	0·742	0·716	0·678	0·638

DISCUSSION.

In obtaining the values of e_0' recorded above, it is assumed that the electrode potential is determined by the equilibrium (1). Other electromotively active reducing substances

besides nitrous acid are probably present at appreciable concentrations in the solutions, but in so far as they are in true equilibrium with nitric and nitrous acids their presence will not affect the validity of relations (2) and (3). On the other hand, if such substances affect the accuracy of the analytical determination of nitrous acid, the interpretation of the experimental results in terms of these relations becomes more difficult. Actually, the only substances likely to produce an appreciable effect of this kind are nitrogen trioxide and peroxide, the latter existing in the solutions in accordance with the equilibria

$$HNO_3 + HNO_2 \rightleftharpoons H_2O +$$
$$(N_2O_4 \rightleftharpoons 2NO_2) \quad . \quad . \quad (4)$$
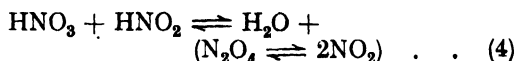
It can be shown, however, that for solutions of specified nitric acid concentration, the error in the determination of nitrous acid due to the reaction $2NO_2 + PbO_2 = Pb(NO_3)_2$ will cause a deviation of $0.0296/\sqrt{1 + kc_{HNO_2}}$ from the theoretical slope of the e–log c_{HNO_2} line, where c_{HNO_2} is the apparent nitrous acid concentration corresponding to the weight of lead sulphate obtained, and k is a constant which involves the equilibrium constants of (4) and the ratio $[HNO_3]/[H_2O]$ for the given nitric acid solution. This deviation evidently decreases with increase in c_{HNO_2}. Actually, however, the experimental points agree closely with the theoretical slope
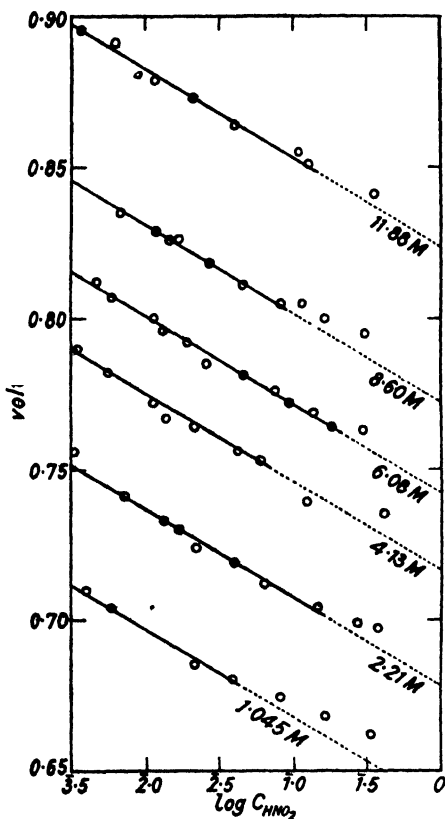
of the e–log c_{HNO_2} lines over a considerable range extending to the lowest values of c_{HNO_2} investigated. It would seem, therefore, that any deviation due to this cause must occur in the region of still lower values of c_{HNO_2}. On the other hand, the presence of nitrogen trioxide in equilibrium with nitrous acid will cause a deviation which

increases with c_{HNO_3}, and is probably partly responsible for the deviations actually observed at higher values of c_{HNO_3}. Nevertheless, although the presence of nitrogen peroxide and trioxide may not cause any deviation from the theoretical slope of the lines in the lower part of the concentration range investigated, it may, of course, affect the *positions* of these lines and hence the values of e_0'. Hence, values of e_0' may not be true oxidation–reduction potentials for the simple system nitric–nitrous acid. They should, however, afford a relative measure of the oxidising tendencies of nitric acid solutions of various concentrations with respect to reactions in which nitric acid is reduced to nitrous acid and such concentrations of nitrogen peroxide and trioxide as may exist in equilibrium with it. Values of e_0' are therefore referred to as *relative oxidation potentials* of the nitric acid solutions.

The actual deviations of the e–log c_{HNO_3} lines from the rectilinear form at high values of c_{HNO_3} are attributed partly to the presence of nitrogen trioxide and partly to divergencies between the molar concentration and activity of nitrous acid, which must be expected to become notable in this range, especially since such solutions also contain considerable amounts of sodium nitrate (derived from the nitrite added) which may affect the activities of both nitric and nitrous acids.

As regards the variation of the relative oxidation potential, e_0', with the molar concentration of nitric acid, c_{HNO_3}, the graph of e_0' against log c_{HNO_3} gives a line which is definitely curved, e_0' increasing more rapidly with log c_{HNO_3} at higher values of the latter. A much less notable curvature is obtained if e_0' is plotted against log p_{HNO_3}, where p_{HNO_3} is the partial pressure of nitric acid over solutions of the various nitric acid concentrations, a quantity which should be proportional to the activity of the acid in these solutions. The curvature disappears entirely if $e_0' + 0.0296$ log $[H_2O]$ be plotted against log p_{HNO_3}, where $[H_2O]$, the activity of water in the solutions, is measured by the ratio of the partial pressure of water, p_{H_2O}, over solutions of the various nitric acid concentrations to that over pure water at the same temperature. Using data for p_{HNO_3} and p_{H_2O} obtained by Taylor at 25° (*Ind. Eng. Chem.*, 1925, **17**, 633) and by Klemenc and Nagel at 12·5° and 30° (*Z. anorg. Chem.*, 1926, **155**, 257), the latter being graphically interpolated to give values at 25°, the empirical relation

$$e_0' + 0.0296 \log [H_2O] = 0.817 + 0.064 \log p_{HNO_3}$$

is found to be obeyed within the limits of probable error over the whole concentration range of nitric acid solutions investigated. The accompanying table shows this for round concentrations of nitric acid at 25°, the values of e_0' being obtained by interpolation from the e_0'–log c_{HNO_3} curve.

HNO$_3$, g.-mol./l.	e_0' (volt).		log p_{HNO_3}.	log p_{H_2O}.	$y = e_0' + 0.0296 \log [H_2O]$.	$y - 0.064 \log p_{HNO_3}$.
2	0.673	K	− 2·27	1·33	0·672	0·818
4	0.714	K	− 1·63	1·28	0·711	0·815
6	0.741	K	− 1·27	1·22	0·736	0·817
8	0.765	{ K	− 0·95	1·12	0·758	0·819
		{ T	− 0·91	1·17	0·759	0·820
10	0.789	{ K	− 0·56	1·01	0·778	0·814
		{ T	− 0·49	1·05	0·779	0·815
12	0.826	{ K	− 0·05	0·86	0·811	0·814
		{ T	− 0·14	0·93	0·813	0·822
					Mean	0·817

T = Taylor; K = Klemenc and Nagel.

The general form of this empirical relation is compatible with the theoretical expression

$$e_0' + 0.0296 \log [H_2O] = e_0 + 0.0296 \log [HNO_3][H^{\cdot}]^2$$

obtained by eliminating $[HNO_2]$ from relations (2) and (3). Beyond this, it is not possible to go at present owing to lack of knowledge regarding liquid-junction potentials, the activity of the hydrogen ion in the more concentrated nitric acid solutions, and possible effects of nitrogen peroxide and trioxide on the relative oxidation potential. It may be noted, however, that the value + 0·649 of e_0' for 1·29M-nitric acid, in which, according to the data of Lewis and Randall ("Thermodynamics," 1923, p. 567) and Abel, Redlich, and Lengyel

(*Z. physikal. Chem.*, 1928, **182**, 189), the stoicheiometric activity of nitric acid should be practically unity, corresponds very closely with the value $+ 0.93_5$ on the hydrogen scale ($+ 0.65_2$ against the normal calomel electrode) calculated by Pick (*Z. Elektrochem.*, 1920, **26**, 182) for the standard potential of the equilibrium $NO_3' + 3H^{\cdot} + 2\ominus \rightleftharpoons H_2O + HNO_2$, which is identical with equilibrium (1) in respect of activity relations.

From the values of e_0' obtained above, it appears that the nitric acid solutions used by Ihle for his potential measurements (*loc. cit.*) contained 10^{-4} to 4×10^{-3} g.-mol. of nitrous acid or equivalent reducing substance per litre, whereas the specially treated solutions used by one of us (*loc. cit.*) for cathode-potential measurements contained only about 10^{-5} g.-mol. per litre.

IMPERIAL COLLEGE, LONDON, S.W. 7.   [*Received, December 17th,* 1934.]

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29. *The Crystal Form of Anhydrous Citric Acid.*

By G. M. BENNETT and JOHN L. YUILL.

IT has long been known that, in addition to the familiar monohydrate of citric acid, which crystallises in the orthorhombic system (Groth, " Chemische Kristallographie," iii, p. 475), the acid may be obtained anhydrous by cooling its hot concentrated aqueous solutions (Buchner and Witter, *Ber.*, 1892, **25**, 1159; Meyer, *Ber.*, 1903, **36**, 3599). As no crystallographic description of this substance has been recorded, we have now examined it goniometrically. Suitable crystals were obtained with considerable difficulty.

Anhydrous citric acid crystallises in the holohedral class of the monoclinic system with axial angle $\beta = 99° 7'$ and axial ratios $a : b : c = 1.936 : 1 : 1.150$. Barker classification angles: $a(100) : m(110) = 62° 23'$, $c(001) : r(101) = 29° 25'$, $r(101) : a(100) = 51° 28'$, and $b(010) : q(011) = 41° 23'$. The following is a list of the forms observed and the mean angular measurements obtained with a two-circle goniometer from five selected crystals:

	a(100).	c(001).	R(Ī01).	s(Ī01).	m(110)	k(121)
ρ	90° 0'	90° 0'	90° 0'	90° 0'	*27° 37'	*29° 4'
ϕ	0° 0'	*80° 53'	111° 5'	134° 5'	0° 27'	*51° 28'

The usual habit of the crystals is as shown in the annexed figure with R and s small, the latter being sometimes absent.

The substance has a low positive double refraction. In convergent polarised light, one optic axis is seen emerging nearly perpendicular to the face a, and the second through the face R, the optic axial plane being parallel to the plane (010).

The density of the crystals, found by flotation in a mixture of acetylene tetrabromide and light petroleum, is $d_4^{18°}$ (vac.) $= 1.665$, and the m. p. 156—157° (corr.).

In view of the discussion which formerly arose as to the conditions under which the anhydrous and the hydrated form may be deposited from solution (*locc. cit.*), we have now determined the transition point. Observations were made of the cooling curve of pure citric acid (thrice recrystallised from distilled water) in the presence of water.

The apparent temperature of arrest was somewhat sensitive to variations in the temperature of the bath surrounding the air jacket—presumably owing to a low value of the heat of transformation. Care was therefore taken to keep the outer bath as near to the observed temperature as possible, and the temperature of arrest was taken both during heating and cooling. Found: with falling temperature 36·15°; with rising temperature 36·45°; mean value *36·3°*. The thermometer, graduated in 0·1°, was checked by observing the transition point of sodium sulphate decahydrate (Found: 32·4°; Richards and Wells, *Z. physikal. Chem.*, 1903, **48**, 465, give 32·38°).

THE UNIVERSITY, SHEFFIELD.   [*Received, December 29th,* 1934.]
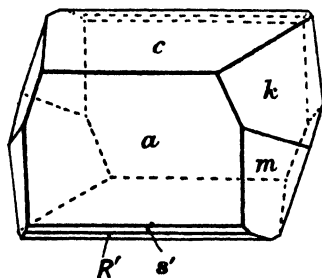
30. *The Influence of Variations in Structure on the Reactivity of an Alcohol with Hydrobromic Acid.*

By G. M. BENNETT and FREDERICK M. REYNOLDS.

AN extensive survey of the reactivities of alcohols with acetic acid was made by Menschutkin (*Annalen*, 1879, **195**, 334; **197**, 193; *Ann. Chim. Phys.*, 1881, **23**, 14), comparison being made of that proportion of the ultimate (equilibrium) yield of ester which was produced from each alcohol in the first hour of reaction. In a later study, the same author found (*Z. physikal. Chem.*, 1887, **1**, 611) that the reaction of an alcohol with acetic anhydride is accurately bimolecular (compare also Moelwyn-Hughes and Rolfe, J., 1932, 241) and various types of alcohol were again compared. In more recent years, Norris and his co-workers have studied the reactions between alcohols and p-nitrobenzoyl chloride, benzhydryl chloride, and its substituted derivatives (*J. Amer. Chem. Soc.*, 1925, **47**, 837; 1927, **49**, 2640; 1928, **50**, 1795, *et seq.*). For the reaction with nitrobenzoyl chloride, constant velocity coefficients were not obtained, and the explanation of this as being due to several successive reactions has since been elaborated (Meisenheimer and Schmidt, *Annalen*, 1929, **475**, 157).

The reaction between alcohols and hydrogen bromide, with or without the presence of water, has already been examined by Norris (*Z. physikal. Chem.*, 1927, **130**, 660; *Rec. trav. chim.*, 1929, **48**, 885) and by Levene and Rothen (*J. Biol. Chem.*, 1929, **81**, 359), who have shown that water, present originally or formed during the reaction, has a large influence on the velocity. Their figures, however, are open to criticism, for constant velocity coefficients were usually not obtained; in some instances the reaction mixtures separated into two phases during the process, and the reverse reaction was not always sufficiently taken into consideration.

Comparative velocity measurements have now been made of the reaction with a series of ten primary and two secondary alcohols, nine homologous aliphatic glycols, four glycol chlorohydrins, and seven aryloxy-alcohols. In addition, comparable figures for a series of nine phenylthio-alcohols are available from a previous study. With certain more reactive substances, such as *tert.*-butyl alcohol and aromatic alcohols, accurate measurements have been prevented by the occurrence of subsidiary reactions. These and some other substances have been examined by means of semi-quantitative or qualitative comparative tests.

Method of Measurement and Kinetics of the Reaction.—The measurements were carried out by the method of Bennett and Mosses (J., 1931, 2956), phenol being used as solvent. Some solvent is clearly necessary for the examination of a large variety of substances, often available in relatively small amounts, under strictly comparable conditions in similar homogeneous systems. The alternative solvent, acetic acid, was rejected, as some esterification of it seemed inevitable. When, in the course of the work, ethylene chlorohydrin and *iso*butyl alcohol were found to have extremely small velocities of reaction with hydrobromic acid (see pp. 134, 135), it seemed possible that these substances might be used as solvents. With the more reactive alcohols, such as *tert.*-butyl alcohol, however, accurate measurements were found to be impossible in these solvents, for the reaction appeared to stop at an early stage owing to the liberation of hydrogen bromide in a subsidiary reaction involving the formation of an ether (cf. p. 132).

In order to simplify the results, the reagents were used in the approximate molecular ratios of alcohol : hydrogen bromide : water $= 1 : 2 : 10$. This constitutes an attempt to isolate the reaction with respect to water, the concentration of which has a large influence on the reaction velocity. Complexities discussed by earlier workers (*e.g.*, Price, J., 1901, **79**, 303) had also been taken into account. The actual molecular proportion of water chosen was necessarily limited by the solubilities of some of the substances studied.

Although it was not the main object of this investigation to examine the equilibrium of the reversible reaction in detail, it was necessary to consider the evidence on this point and also to make a careful search for any subsidiary reactions other than the reversal (hydrolysis of the halide). The work of Kilpi (*Z. physikal. Chem.*, 1914, **86**, 427; 1929,

141, 424; **142**, 195; 1933, **166**, *A*, 285) on the interaction of hydrogen chloride and ethyl or *n*-propyl alcohol has sufficiently confirmed the applicability of the equation for a reversible reaction under the conditions used by him, the alcohol being present in excess. The general equation was applied by Bennett and Mosses (*loc. cit.*) and has been used in this work, but it may be pointed out that, owing to the conditions deliberately chosen, the velocity coefficients obtained would have been altered only slightly if the reverse reaction had been entirely neglected and values of the initial velocity calculated; *e.g.*, for *iso*propyl alcohol (in which the reaction was followed to an approximate equilibrium), a k_1 was found to be 0·0292, as compared with 0·0273 if the reverse reaction is neglected. In general, the forward reaction is 15—30 times as fast as the hydrolysis, so the error caused by taking the mean coefficient over the first hour at 80° and neglecting the latter would be of the order of 5—10%.

The reaction was followed to a point near equilibrium only in the cases of the more reactive alcohols for which measurements are recorded, *viz.*, methyl, *iso*propyl, and *sec.*-butyl. In these instances, the observed limiting concentration inserted in the equation gave coefficients satisfactorily constant over the main range of the reaction, so the attainment of an approximate equilibrium is confirmed. In other cases, the equilibrium was not approached, and the coefficients were calculated by choosing a figure for $t = \infty$ which led to constant values. Here, again, the exact figure chosen has a minor influence on the magnitude of the calculated velocity. Taking the mean value of the constant coefficients for the earlier part of the reaction, we consider that the figures should not be in error by as much as 5%.

Subsidiary Reactions.—When the ω-hydroxy-sulphides were examined, an important secondary reaction involving self-addition of the generated bromo-sulphide was in evidence. This reaction was clearly impossible with the compounds used in the present work, and it had been hoped that all subsidiary reactions might be avoided. There are, however, two at least which require consideration, *viz.*, a substitution of the aromatic nucleus of the phenol by the alkyl bromide, $RBr + C_6H_5 \cdot OH \longrightarrow C_6H_4R \cdot OH + HBr$, and the formation of an ether in the sense $R \cdot Br + R' \cdot OH \longrightarrow R \cdot O \cdot R' + HBr$, where R may be the same as, or different from, R'. Many experiments were made expressly to ascertain the extent of the interference of these reactions.

Both these reactions are negligible with the primary aliphatic alcohols. With the secondary alcohols, the nuclear condensation can be detected, but is a complication of an entirely lower order of magnitude. With *tert.*-butyl alcohol and triphenylcarbinol, this reaction is prominent, the *p*-substituted phenol being formed in quantity. Exact measurements were here not attempted, but qualitative conclusions can nevertheless be deduced.

As regards the second of these subsidiary reactions, Villiers's work (*Compt. rend.*, 1903, **136**, 1551) had indicated that the presence of several molecular proportions of water in excess in our mixtures would suppress it. Norris (*locc. cit.*) states that this reaction was observable at the end of his experiments, but gives no details of any tests made to delimit the occurrence. Consideration of this reaction $R \cdot Br + R'OH \longrightarrow R \cdot O \cdot R' + HBr$ shows that the bromide will react with increasing ease according as R is primary, secondary, or tertiary, whilst the alcohol will react with increasing readiness in the reverse order (cf. discussion, p. 135, and the work of Norris and others, *locc. cit.*). Consequently this reaction could not be as much favoured in our experiments (where R = R' in all cases except when ethylene chlorohydrin or *iso*butyl alcohol was used as solvent) as it would be in the mutual action of a secondary bromide with a primary alcohol. A direct test was therefore made with *iso*propyl bromide and *n*-butyl alcohol, and the ether formation found to be negligible under the conditions of our measurements. It is, however, entirely consistent with the above view that the same reaction should occur extensively when an attempt was made to follow the reaction between hydrobromic acid and *tert.*-butyl alcohol in ethylene chlorohydrin as solvent.

The Aliphatic Glycols.—Comparative reactivities in a series of normal glycols were assessed by a graphical method, the velocity being computed from the value of the initial rate of fall of concentration of hydrogen bromide, divided by 2 on account of the presence

of two hydroxyl groups per molecule of glycol. The method is a little less accurate, but gives results in fair agreement with those calculated when the two methods are applied in a simple case; *e.g.*, data for the velocity of the reaction of *n*-propyl alcohol were : at 80·6° 0·00311 (graphically), 0·00286 (from equation); at 92·3°, 0·0123 and 0·0121, respectively. In view of this lower degree of precision, we have not attempted to deduce approximate values of the activation energies concerned.

Examination of the more Reactive Alcohols, and the Condensation of Alkyl Halides with Phenol.—General experience and several published statements (Henry, *Bull. Acad. roy. Belg.*, 1906, **261**; Norris, Watt, and Thomas, *J. Amer. Chem. Soc.*, 1916, **38**, 1071) indicated that a tertiary aliphatic alcohol would react much faster with hydrobromic acid than do secondary or primary alcohols, as would, moreover, be expected as a result of the operation of the known inductive effects of the alkyl groups. Yet when an experiment was conducted with *tert.*-butyl alcohol in phenol solution at 80°, no fall in concentration of the acid was observed after either a few minutes or several hours. It was, however, found that the reaction mixture contained *p-tert.*-butylphenol in quantity, the apparent lack of reactivity being thus clearly due to a liberation of hydrogen bromide in the nuclear condensation.

A similar apparent failure to react was shown by triphenylcarbinol, benzyl alcohol, and *p*-chloro- and *p*-bromo-benzyl alcohols, and the formation of the substituted phenol was confirmed in the first two of these cases.

In the attempt to determine the comparative reactivities of these alcohols, a further difficulty arises from the fact that the speed of hydrolysis of *tert.*-butyl bromide is so great that it liberates its equivalent of acid when shaken with cold water for 10 minutes (compare Michael and Leupold, *Annalen*, 1911, **379**, 263; Michael and Zeidler, *ibid.*, 1912, **393**, 81). This makes the alkalimetric method inaccurate : by rapid working an end-point is observable which must, however, be regarded as erring in the direction of hydrolysis. With *tert.*-butyl alcohol at lower temperatures, the forward reaction and its subsequent reversal by the secondary nuclear condensation became evident. At 40° it was thus proved that the tertiary alcohol reacts with hydrogen bromide at least 100 times as fast as methyl alcohol. Comparative tests in ethylene chlorohydrin or *iso*butyl alcohol as solvent showed that the velocities of reaction with hydrogen bromide diminish in the order tertiary > secondary > primary alcohols.

No reaction can be detected between phenol and primary alkyl bromides at 100°, but with *iso*propyl and *sec.*-butyl bromides, although the liberation of hydrogen bromide is very slow, it can be followed at 80° or 90°. The results, and those obtained by heating the corresponding alcohols with phenolic hydrobromic acid for long periods, show that this secondary reaction is negligible compared with the forward reaction of the acid on the alcohol.

tert.-Butyl bromide reacts quantitatively with phenol in a few minutes at 90°, but the reaction is slow at 50°. The addition of a little zinc chloride greatly accelerates the reaction with tertiary or secondary bromides, but not that of primary alkyl bromides. Triphenylmethyl bromide condenses rapidly with phenol.

Variation of the Velocity Coefficients with Composition of the Reaction Mixture.—The velocity of the reaction is not independent of the initial concentrations, being particularly susceptible to variations in the proportion of water (cf. Norris and others, *locc. cit.*). A series of determinations with *n*- and *iso*-propyl alcohols showed that the velocity coefficient is increased by an increased initial concentration of hydrogen bromide, and depressed by an increased initial concentration of water or of hydrogen bromide and water simultaneously when maintained in the same ratio. An increase in the initial proportion of alcohol also causes a fall in the velocity. This may be ascribed to a solvent effect, for the increased ratio of alcohol to phenol as solvent will alter the cohesion of the mixture. This is confirmed by the observation that addition of *iso*butyl alcohol (which has a relatively negligible reaction velocity itself) caused a large reduction in the velocity coefficient for *iso*propyl alcohol.

The results of the measurements are given in Tables I—III, in which k_1 is the velocity coefficient of the forward reaction, E the approximate activation energy of the reaction, and K the equilibrium constant.

TABLE I.

Velocities of Reaction of Alcohols with Hydrogen Bromide in Phenol.

(Values of k_1 for forward reaction; time in mins.; concn. in mols./l. D = Maximum deviation, %, of k_1 from the mean.)

Alcohol.	$k_1 \times 10^4$ 80·3°.	92·0°.	D.	K.	E, kg.-cals.	Alcohol.	$k_1 \times 10^4$ 80·3°.	92·0°.	D.	K.	E, kg.-cals.
Methyl	178		3·4	31·0	26·6	n-Heptyl	29·2		2·3	16·1	30·1
		603	3·7	31·6				116	1·9	17·3	
Ethyl	31·7		1·3	19·6	31·3	n-Octyl	28·6		1·7	20·2	29·5
		132	0·7	17·1				110	3·4	20·6	
n-Propyl	27·5		4·4	22·7	31·7	(Cetyl	28·5)				
		117	3·4	20·5							
n-Butyl	28·5		4·6	21·9	29·6	isoButyl	3·58		5·6	6·4	28·4
		110	1·8	22·5				13·1	4·3	10·6	
n-Amyl	28·5		2·7	19·3	30·6	sec.-Butyl 173			5·8	18·3	29·9
		116	3·7	23·4				678	2·6	19·9	
n-Hexyl	28·5		5·0	24·2	30·9	isoPropyl	72·9		1·9	13·5	30·1
		117	3·5	23·9				289	8·2	13·4	

TABLE II.

ω-Phenoxy-alcohols.

	$k_1 \times 10^4$ 86·0°.	97·0°.	D.	K.	E, kg.-cals.		$k_1 \times 10^4$ 86·0°.	97·0°.	D.	K.	E, kg.-cals.
β-Phenoxyethyl	—	7·86	4·7	50·3	—	δ-Phenoxybutyl	109		2·8	20·6	
γ-Phenoxypropyl	27·7		5·1	19·7				351	3·7	86·3	25·8
		94·1	3·4	18·9	24·3	(n-Octyl		191)			

Glycol chlorohydrins (ω-chloro-alcohols).

	$k_1 \times 10^4$ (97·0°).	D.	K.		$k_1 \times 10^4$ (97·0°).	D.	K.
Ethylene	zero	—	—	Heptamethylene	171	2·9	46·8
Trimethylene	37·8	2·4	22·4	(n-Octyl alcohol	191)		
Tetramethylene	75·1	6·3	19·6				

β-Aryloxyethyl alcohols, $C_6H_4X \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$.

X.	$k_1 \times 10^5$ (97·0°).	D.	K.	X.	$k_1 \times 10^5$ (97·0°).	D.	K.
H	78·6	4·7	—	p-CH₃	102	6·4	48·0
o-CH₃	86·8	3·1	44·0	p-Cl	55·9	3·2	59·6
m-CH₃	81·8	3·7	50·2				

TABLE III.

n-*Glycols.*

	$k_1 \times 10^5$ 75·9°.	85·0°.		$k_1 \times 10^5$ 75·9°.	85·0°.		$k_1 \times 10^5$ 75·9°.	85·0°.
Ethylene	9·0	30·5	Pentamethylene	237	632	Octamethylene	149	308
Trimethylene ...	41	187	Hexamethylene	131	353	Nonamethylene	153	371
Tetramethylene	273	1340	Heptamethylene	122	384	Decamethylene	138	—

Discussion of Results.—The comparative figures for the n-aliphatic alcohols fall on a smooth curve, the values diminishing from methyl to propyl and thereafter remaining constant. The activation energy is approximately constant in this series at 30,500 cals., but that for methyl alcohol is smaller, 26,600 cals. The two secondary alcohols are more reactive than their primary isomerides, but the reactivity of *iso*butyl alcohol is much lower. The results for the normal alcohols are in general agreement with those of Norris (*loc. cit.*) in his series B, but they do not support the somewhat irregular variation found by him as the homologous series is ascended. It is probable that our method of experiment has been more successful in eliminating variable influences of solvent and water in the reaction.

General Influence of Substituents on the Reaction.—The reaction of an alcohol with hydrogen bromide may be represented as proceeding in two stages : (*a*) the formation of the oxonium complex $R\overset{\oplus}{O}H_2]\overset{\ominus}{Br}$, and (*b*) the elimination of water, giving $RBr + H_2O$. Of these, process (*a*) must be facilitated by accession of electrons to the hydroxyl group. The

same should be true of (*b*) provided that the R–O bond be broken before the bromion becomes attached to R. The opposite effect should, on the other hand, be found for any reaction in which the hydroxyl group is split between oxygen and hydrogen, thus R·O–⊦–H, the ultimate difference in the two types of reaction being that hydroxyl is separated from the molecule of the alcohol in the former and hydrogen in the latter. The second of these types includes the reactions R·OH + Ar·COCl ⟶ R·O·CO·Ar + HCl and ROH + CHAr₂Cl ⟶ R·O·CHAr₂ + HCl studied by Norris and others (*locc. cit.*), and it is therefore satisfactory to find that the order of relative reactivity of alcohols, primary < secondary < tertiary, which we find for the reaction with hydrobromic acid is the opposite of that observed by Norris for the reactions of the second type. As regards the reactions ROH + AcOH ⟶ ROAc + H₂O and ROH + Ac₂O ⟶ ROAc + AcOH, studied by Men-schutkin, there can be little doubt that the division of the alcohol group is here also between oxygen and hydrogen RO–⊦–H. In the case of phenol (Menschutkin), this is the only reason-able possibility. Moreover, the reaction between alcohol and acetic acid is reversible, and for both acid and alkaline hydrolysis it has been clearly proved that the oxygen atom remains attached to the alkyl group of the alcohol throughout (see *e.g.*, Ingold and Ingold, J., 1932, 756). Polanyi and Szabo have recently described an independent demonstration of the point depending on the use of water with a relatively high proportion of the isotope O¹⁸ in the hydrolysis (*Trans. Faraday Soc.*, 1934, **30**, 508). Consequently, as would be expected, the three classes of alcohol are ranged in Menschutkin's lists in the order primary > secondary > tertiary : indeed, the comparison of this order with those of Norris and of the present investigation might conversely be regarded as yet another indication of the mode of division of the C·O·H group in its reaction with acetic acid.

The view of the reaction between hydrobromic acid and an alcohol given above, *viz.*, that it is of type A (Ingold and Rothstein, J., 1928, 1217), is entirely confirmed by the observed influence of substituents on the reactivity of an alcohol, for this is not only increased by substitution of alkyl groups for hydrogen but it is greatly decreased by the introduction of a chlorine atom or a nitro-group into an alcohol, β-chloro- and β-nitro-ethyl alcohols being practically inert. This influence diminishes as the distance of the substituent from the hydroxyl group increases, as the following observed inequalities in reactivity of alcohols show : β-chloroethyl < γ-chloropropyl ≪ *n*-propyl, and β-nitroethyl < γ-nitro-propyl ≪ *n*-propyl.

Qualitative observations (Henry, *Compt. rend.*, 1906, **142**, 129) illustrate the retarding effect of an adjacent chlorine atom on the reaction of a hydroxyl group with hydrogen chloride. Henry found that, whereas cold *tert.*-butyl alcohol reacts instantaneously with hydrogen chloride, its monochloro-substituted derivative will only react at 100°, whilst its di- and tri-chloro-derivatives are completely inert. This influence of a chlorine atom was much smaller when it was inserted in a position more remote from the hydroxyl group, as in the alcohol CMe₂(OH)·CH₂·CH₂Cl. The cyano-group also has a strong influence in depressing such a reaction, for acetonecyanohydrin, CMe₂(OH)·CN, fails to react with respect to its hydroxyl group. The carbethoxy-group has a similar but weaker effect, as illustrated by the inertness of the hydroxy-ester CEt₂(OH)·CO₂Et towards hydrogen chloride.

In the present study, observations made on two series of substituted alcohols containing aromatic groups further demonstrate the direction of the influence of polar groups. For instance, in the β-aryloxyethyl alcohols we have the descending order of reactivities *p*-tolyl > *o*-tolyl > *m*-tolyl > phenyl > *p*-chlorophenyl; and approximate comparative tests, made with some β-arylthioethyl alcohols, prepared for another investigation, of which sufficient quantities were not available for complete velocity measurements, show that for the substances Ar·S·CH₂·CH₂·OH the reactivity of the hydroxyl group with hydrogen bromide diminishes in the order *p*-methoxyphenyl > phenyl > *p*-bromophenyl > *p*-nitro-phenyl and *s*-trichlorophenyl > 2 : 4-dinitrophenyl. In all these cases the retarding effect of an electron-attracting group or the acceleration due to an electron-repelling group is illustrated. In view of the well-known tendency for phenyl to act as an " electron source " on demand in conjugated systems, the high reactivity of benzyl alcohols and of triphenyl-carbinol is also consistent with this view.

Steric-hindrance Effects.—The low velocities of esterification of secondary and tertiary alcohols by acetic acid have been commonly regarded as the result of steric hindrance : the above discussion makes it clear that the actual variations in reaction velocity are partly due to the operation of polar factors, for these alone would suffice to give a qualitative explanation of the behaviour of these alcohols towards both acetic and hydrobromic acid. The possibility remains that steric hindrance is also present. The low velocity of reaction of *tert.*-butyl alcohol with acetic acid may be caused by the methyl groups acting both by their inductive effects and by their screening of the hydroxyl group; and the high reactivity of the same alcohol with hydrobromic acid might represent the result of the polar factor, any screening effect of the methyl groups being outweighed. It seems probable, however, that steric hindrance would not affect the latter reaction. If the action proceeds by the disruption of an oxonium complex rapidly but reversibly formed, the effect of screening would only appear if it influenced the position of equilibrium. This equilibrium, determined in the main by polar factors, might be affected as regards its velocity of attainment, but not as regards its position, by steric hindrance, for the following reason. The hydrogen ion can only approach or leave the complex in combined form (*i.e.*, as hydroxonium ion or other solvated ion or as hydrogen bromide), so the formation and dissociation of this complex must be similar bimolecular processes equally influenced by any steric hindrance which arises (compare the ionic dissociation of acids; Lapworth and Manske, J., 1928, 2534; Shoppee, J., 1930, 971).

A further indication of an influence which appears to be polar rather than steric can be found in the data concerning alcohols with carbon chains branched at C_β. From Menschutkin's figures, with an addition by Tissier (*Ann. Chim. Phys.*, 1893, **29**, 340), the speed of reaction with acetic acid is slightly depressed in *iso*butyl alcohol (comparative velocity 44·4) and *tert.*-butylcarbinol, $CMe_3 \cdot CH_2 \cdot OH$ (40·5), as compared with *n*-butyl alcohol (46·8), which must represent the combined effects of screening (if any) and some transmitted polar effect. In the reaction with hydrobromic acid, on the other hand, we find a striking depression of reactivity in *iso*butyl alcohol ($k_1 = 0.000358$, as compared with 0·00285 for *n*-butyl alcohol : the difference is also clearly shown by Norris's figures). Even if steric hindrance were here involved, it would not be expected to be more effective than in the reaction with acetic acid, so that some other explanation seems necessary. The case is reminiscent of the definitely increased acidity of those aliphatic acids which have terminal methyl groups in a position to approach the carboxyl group in space (Bennett and Mosses, J., 1930, 2364). In *iso*butyl alcohol the basic property of the hydroxyl group, and consequently the speed of the reaction with hydrobromic acid, may be diminished for a similar reason, *viz.*, the influence of the external field of the methyl groups.

The Influence of a Terminal Substituent on a Hydroxyl Group separated from it by a Growing Hydrocarbon Chain.—In a previous paper (Bennett and Mosses, *loc. cit.*) the reactivity of a hydroxyl group was shown to be greatly enhanced by the presence of a sulphur atom in the β-, δ-, or ε-position to it (separated by 2, 4, or 5 carbon atoms), but depressed if the sulphur atom is in the γ-position, and an explanation based on the steric accessibility of the separated groups was advanced. The present study shows how far these phenomena are repeated when oxygen replaces sulphur. The available data are summarised in Table IV, which records comparative reactivities for the series $X \cdot [CH_2]_n \cdot OH$, where X = H (alcohols), SPh (from the earlier paper), OPh, OH (glycols), and Cl (chlorohydrins). The variation in these series is shown graphically in the fig. the series with X = SPh being, however, omitted, as it was represented graphically in the earlier paper and the differences involved are of a much higher order.

In view of the smallness of the influence which an atom or group can exercise on a hydroxyl group separated from it by a long saturated chain, it was to be expected that the reactivity in these series would tend to similar values when *n* is large, approximating to a value which may be regarded as that of the isolated hydroxyl group $\cdots CH_2 \cdot OH$. In fact, this is found to be the case. Thus the mean value of the reactivity for $SPh \cdot [CH_2]_9 \cdot OH$ and $SPh \cdot [CH_2]_{10} \cdot OH$ at 80·0° is 0·00285 as compared with that for octyl alcohol 0·00276. The velocity coefficients for heptamethylene chlorohydrin and for octyl alcohol at 97° are 0·0171 and 0·0191 respectively. In the series of glycols, the mean figure for those of 6—9

TABLE IV.

Comparative Reactivities in the Series $X \cdot [CH_2]_n \cdot OH$.

X = Temp.	H. 80·3°.	SPh. 80·0°.	OH. 85·0°.	OPh. 97·0°.	Cl. 97·0°.
n = 1	6·24	—	—	—	—
2	1·11	1,160	0·086	0·041	0·00
3	0·96	0·40	0·528	0·49	0·20
4	1·00	289	3·78	1·84	0·39
5	1·00	3·16	1·79	—	—
6	1·00	1·27	1·00	—	—
n = 7	1·02	1·36	1·08	—	0·90
8	1·00	1·32	0·87	—	—
9	—	1·10	1·05	—	—
10	—	0·97	—	—	—
16	1·00	—	—	—	—

carbon atoms is 0·00354 at 85·0° as compared with 0·00498 for octyl alcohol. The discrepancy here is, however, accounted for by the marked influence of the initial concentration of the alcohol in the reaction (p. 133), since an equal *molecular* concentration of the glycols was taken. When hexamethylene glycol was re-examined at half the molecular concentration (*i.e.*, an equivalent concentration of hydroxyl), the value found was 0·00450, which
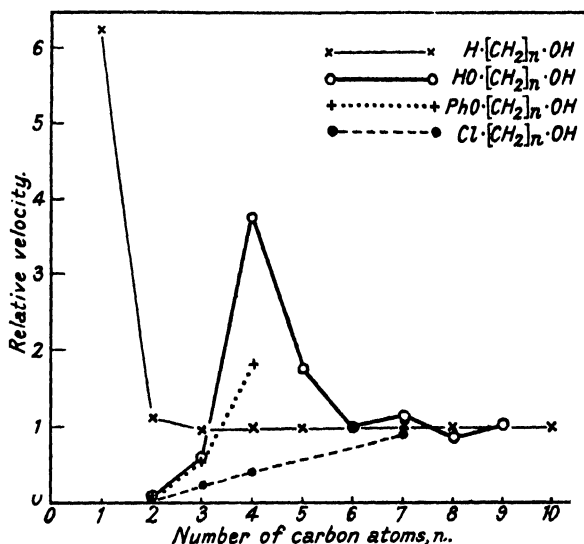
Comparative velocities of the series $X \cdot [CH_2]_n \cdot OH$ *with hydrobromic acid.*

is in closer agreement with that for the long-chain aliphatic alcohol. The comparative figures for the glycols have therefore been calculated by putting the mean value for those of long chain equal to unity.

The special activation of the member $X \cdot [CH_2]_4 \cdot OH$, which was so striking a feature in the phenylthio-alcohol series (X = SPh), is clearly apparent, although in smaller degree, for both the glycols and the phenoxy-alcohols (X = OPh). Moreover, as before, the next higher member, $X \cdot [CH_2]_5 \cdot OH$, of the glycol series is definitely activated. As there is no possibility of the permanent closure of a ring in, *e.g.*, the case of $OPh \cdot [CH_2]_4 \cdot OH$, we thus obtain independent confirmation of activation apart from actual ring-closure (compare the earlier discussion on this point, J., 1930, 2365).

The depressed reactivity of the compound $X \cdot [CH_2]_3 \cdot OH$ found when X = SPh, also appears in the two series with oxygen in place of sulphur (X = OH and OPh), but the high reactivity of the β-phenylthio-alcohol finds no parallel in these series. The following considerations show that these results are consistent with general theory and with the special explanation previously advanced.

The oxygen atom exercises a greater inductive restraint on electrons than sulphur—as is shown by the fact that the acids $Ar \cdot O \cdot CH_2 \cdot CO_2H$ are always stronger than their sulphur analogues $Ar \cdot S \cdot CH_2 \cdot CO_2H$ (Behaghel and Rollmann, *Ber.*, 1929, **62**, 2693). On the other hand, the sulphur atom has a much more pronounced tendency to share its outer electrons,

as in the formation of the alkyl " onium " salts, than oxygen. For this reason, when, in the compounds X·[CH₂]₄·OH and to a smaller extent X·[CH₂]₅·OH, the group X approaches the CH₂OH group and confers on it an enhanced reactivity, the effect is much larger with sulphur than with oxygen. When, on the other hand, X is in the β-position, as in the compounds X·[CH₂]₂·OH, any activation which might arise from the contact of the oxygen atom with the CH₂OH group (i) is of an essentially lower order, for the reason just given; (ii) is reduced by the smaller facility of access of the oxygen than of the sulphur atom to the carbinol group on account of its smaller atomic diameter, and (iii) is outweighed by the much larger inductive deactivating influence of oxygen than of sulphur.

In discussing the reactivities of the phenylthio-alcohols, the alternative possibilities were considered that the activation of the hydroxyl group arose either from the close approach of sulphur and carbinol group in space or from an actual contact, with sharing of electrons during the reaction. We have now compared, not only the glycols and phenoxy-alcohols, but also the chlorohydrins and β- and γ-nitro-alcohols, in which the approach of a chlorine or an oxygen atom respectively to the carbinol group is sterically possible. No indication appears of any increased reactivity with δ-chlorobutyl or γ-nitropropyl alcohol, so it may be concluded that an atom which possesses lone pairs of electrons but has no definite tendency to share them by increasing its covalency does not cause activation by its close approach to the terminal carbinol group. We consequently incline to the view that the special reactivity depends on an actual participation of the sulphur or oxygen atom in the reaction.

Finally, it may also be noted that the observed variation in reaction velocity provides an explanation of the differences found in the ease of preparation of some of the glycol derivatives. For instance, ethylene chlorohydrin is readily obtained from glycol in almost quantitative yield, because the second hydroxyl group is rendered inactive by the first chlorine atom to enter the molecule. With trimethylene glycol, the chlorohydrin is partly attacked by hydrogen chloride, and the yield may be only 60% unless care is taken to secure good mixing of the reactants (Gough and King, J., 1928, 2439). Again, in the reaction between glycols and acetyl chloride (Bogert and Slocum, *J. Amer. Chem. Soc.*, 1924, **46**, 763; Bennett and Heathcoat, J., 1929, 268) for the preparation of the ω-chloroalkyl acetates, the first step is no doubt the formation of the monoacetyl compound of structure OAc·[CH₂]ₙ·OH, which is then acted upon by the liberated hydrogen chloride. The yield in this reaction is remarkably high for the tetramethylene derivative ($n = 4$), which is evidence of a specially high reactivity of the corresponding member of the series of acetoxy-alcohols.

<center>EXPERIMENTAL.</center>

Preparation of Materials.—Alcohols. Specimens of methyl alcohol, (a) from a sample of Merck's acetone-free alcohol and (b) from the hydrolysis of the pure oxalate, were dried over quicklime and fractionated; both had b. p. 64·5—64·7°, $d_4^{16°}$ (vac.) 0·79588, $d_4^{25°}$ (vac.) 0·7877 (compare Dittmar and Fawsitt, *Trans. Roy. Soc. Edin.*, 1889, **33**, 509). *n*-Heptyl and *n*-octyl alcohols were purchased from British Drug Houses Ltd., and once fractionally distilled before use. All the other alcohols were carefully dried over lime, fractionated with an efficient column, and material boiling within 0·3° taken for use. The *n*-amyl alcohol was prepared from *n*-butyl-magnesium bromide (Grignard and Tissier, *Compt. rend.*, 1902, **134**, 107).

Glycols. Ethylene glycol was fractionally distilled, and material of constant b. p. used. Trimethylene glycol was converted in quantity into its dibenzoate, m. p. 57°, which was hydro-lysed, and the regenerated glycol dried and distilled. It was a colourless liquid of sweet smell and taste; b. p. 215°, $d_4^{18°}$ (vac.) 1·0547, $d_4^{25°}$ (vac.) 1·0501.

The glycols of 4, 6, 7, 8, 9, and 10 carbon atoms had been prepared by Bennett and Mosses (*loc. cit.*).

Pentamethylene glycol was prepared by a process which we find much more convenient than any hitherto used, *viz.*, from trimethylene dibromide through ethyl glutarate. To a mixture of sodium cyanide (117 g.) and water (114 c.c.), heated on the steam-bath under a reflux condenser, a solution of trimethylene dibromide (190 g.) in 400 c.c. of alcohol was added (1 hr.), and the heating continued for 30 hrs. The mixture was evaporated, extracted with ethyl acetate (150 c.c.), and the salts washed with the solvent. The dinitrile was recovered from the solution,

and distilled at 145—150°/15 mm. (60 g.); it (36 g.) was then heated for 4 hrs. with alcohol (80 c.c.) and sulphuric acid (90 c.c.). The ethyl glutarate had b. p. 119°/20 mm. (36 g.), and was reduced as described in the earlier paper. The glycol boiled at 134°/19 mm. (7 g. from 19 g. of ester). The net yield of five-carbon from three-carbon glycol was 15% of the calculated.

Glycol chlorohydrins. Ethylene and trimethylene chlorohydrins were carefully fractionated before use. The heptamethylene compound was the specimen previously described and purified as a solid of m. p. 10—11°. Tetramethylene chlorohydrin was prepared as described by Kirner and Richter (*J. Amer. Chem. Soc.*, 1929, **51**, 2503); b.p. 57°/0·5 mm.

Nitro-alcohols. β-Nitroethyl alcohol, prepared as described by Wieland and Sakellarios (*Ber.*, 1920, **53**, 201), had b. p. 75—77°/2 mm., $d_4^{13.8}$ 1·308. γ-Nitropropyl alcohol, prepared by Henry's method (*Bull. Acad. roy. Belg.*, 1897, **33**, 115, 412), had b. p. 125°/25 mm., d_4^{13} 1·175, in agreement with his data.

Aryloxy-alcohols. β-Phenoxyethyl alcohol was prepared by the method of Bentley, Haworth, and Perkin (J., 1896, **69**, 164), and had b. p. 158—160°/80 mm. γ-Phenoxypropyl alcohol was obtained in the same way by heating trimethylene chlorohydrin with sodium phenoxide under reflux in alcohol (3 hrs., yield 50%); b. p. 170°/60 mm. (compare Rudfusz, *J. Amer. Chem. Soc.*, 1919, **41**, 665). δ-Phenoxybutyl alcohol (b. p. 164°/20 mm.) was obtained as described by Marvel and Tanenbaum (*J. Amer. Chem. Soc.*, 1922, **44**, 2645) except that the final reduction was as for the glycols : the yield was similar but the process more convenient. The three tolyloxyethyl alcohols were prepared by Boyd and Marle's method (J., 1914, **105**, 2119), but the *p*-chlorophenoxyethyl alcohol was obtained by heating ethylene chlorohydrin with sodium *p*-chlorophenoxide (10 hrs.).

The β-arylthioethyl alcohols were specimens prepared by Baddeley (J., 1933, 46).

Velocity Measurements in Phenol Solution.—The procedure was that described in the former paper. In a few instances titrations of bromion by means of standard silver solution were made : the results agreed closely with the acidimetric observations.

Details of four experiments are given below, *a*, *b*, and *c* being the initial concentrations (mols./l.) of hydrogen bromide, alcohol, and water; *t* is given in mins.; k_1 was found from the formula given in the former paper. In the last case, the value for $t = \infty$ was found experimentally ; in the other three cases it was calculated (see p. 132).

Ethyl alcohol at 80·3° ($a = 1·17$, $b = 0·515$, $c = 5·31$, $K = 19·6$).

t	0	30	60	140	190	520	(∞
0·089*N*-NaOH, c.c.	23·61	22·54	21·68	19·91	19·12	16·70	16·00)
$k_1 \times 10^5$	—	321	313	317	318	—	Mean 317

n-Propyl alcohol at 80·3° ($a = 1·16$, $b = 0·489$, $c = 5·26$, $K = 22·7$).

t	0	60	110	170	300	390	540	690	(∞
N/10-NaOH, c.c.	23·51	21·73	20·80	19·78	18·51	17·83	17·08	16·58	16·00)
$k_1 \times 10^5$	—	(304)	279	284	263	266	271	287	Mean 275

n-Hexyl alcohol at 79·6° ($a = 1·14$, $b = 0·472$, $c = 5·14$, $K = 24·2$).

t	0	60	120	150	180	210	240	(∞
N/10-NaOH, c.c.	22·08	20·46	19·40	19·10	18·60	18·38	18·05	15·00)
$k_1 \times 10^5$	—	(305)	249	263	274	258	259	Mean 261

Methyl alcohol at 89·9° ($a = 1·19$, $b = 0·495$, $c = 5·35$, $K = 31·6$). Reaction carried to equilibrium.

t	0	5	8	10	12	14	20	30	45	∞
0·1032*N*-NaOH, c.c.	23·10	20·90	19·88	19·35	18·90	18·40	17·51	16·65	15·87	15·30
$k_1 \times 10^4$	—	469	483	496	496	499	487	470	—	
								Mean 487		

Variation of k_1 *with Initial Concentrations of Reactants.*

n-Propyl alcohol at 92·0°.   isoPropyl alcohol at 92·0°.

c.	*a.*	*b.*	$k_1 \times 10^4$.	*c.*	*a.*	*b.*	$k_1 \times 10^4$.	*c.*	*a.*	*b.*	$k_1 \times 10^4$.
4·86	1·16	0·486	130	4·76	1·17	0·481	446	6·19	1·48	0·482	289
5·26	1·17	0·491	117	5·12	1·13	0·695	236	6·35	1·52	0·153	362
6·16	1·14	0·472	67	5·27	1·17	0·481	289	5·65	1·35	0·442	137 *
6·20	1·48	0·486	93	6·13	1·13	0·468	167	5·57	1·33	1·750	80·9

* 2 G. *iso*butyl alcohol in 25 g. phenol added.

Comparison of Some β-*Arylthioethyl Alcohols*, Ar·S·CH₂·CH₂·OH.—These substances were compared as follows : 0·001 mol. of each was added to 2·00 c.c. of a standard phenolic hydro-

bromic acid solution as used in the velocity measurements, and the fall in titre in 10 mins. at 41° observed. The results, expressed in c.c. of $N/10$-alkali, may be taken as approximate relative initial velocities of reaction with hydrobromic acid under these conditions :

Substituent	p-MeO	H	p-Br	p-NO$_2$	s-Cl$_2$	2 : 4-(NO$_2$)$_2$
Reactivity	4·3	2·2	1·0	0·2	0·2	0·0

Action of Hydrobromic Acid on the Nitro-alcohols.—Accurate measurements are not recorded for the reaction velocities of the nitro-alcohols, because the mixtures darkened on heating. It was found, however, that β-nitroethyl alcohol had not reacted to a measurable extent after 1 hr. at 92°, and that the progress of the reaction of γ-nitropropyl alcohol at 92° is certainly less than half that for *n*-propyl alcohol under the same conditions.

Subsidiary Reactions.—(1) *Nuclear condensation.* The titre of a mixture of *tert.*-butyl alcohol and phenolic hydrogen bromide did not change when it was heated at 80°, but dilution of the mixture yielded *p-tert.*-butylphenol, fine needles, m. p. 98° from light petroleum. The benzoate, m. p. 82°, was analysed (Found : C, 79·8; H, 7·0. Calc. : C, 80·2; H, 7·1%). At 40° an initial rapid fall in concentration of hydrogen bromide was followed by an increase.

The course of the reaction of benzyl alcohol at 80° as revealed by titration was similar to the foregoing at 40°. That nuclear condensation occurs in absence of catalysts was confirmed by heating phenol in excess on the steam-bath with benzyl bromide for 1 hr., removing unchanged materials in a current of steam, collecting the oil in ether, and distilling. The fraction of b. p. 310° (uncorr.) solidified and was mainly *p*-benzylphenol, m. p. 83°, from light petroleum (Found : C, 84·5; H, 6·7. Calc. : C, 84·8; H, 6·6%).

The nuclear condensation reaction was also detected in the velocity measurements with *iso*propyl and *sec.*-butyl alcohols as a steady slow drift of the concentration of hydrobromic acid following the initial reaction to an approximate equilibrium.

The experimental figures given below show that this subsidiary reaction is here of an entirely lower order than the main reaction. The observed drift represents, not only the hydrogen bromide liberated in the nuclear condensation, but the combined result of this together with some readjustment of the equilibrium in the main reaction. It can be readily shown that in the case of *sec.*-butyl alcohol at 80°, if the equilibrium were kept exactly readjusted throughout, the observed change in concentration of hydrobromic acid would be reduced by about 30%, and the total error in k_1 due to this subsidiary reaction cannot be more than that which would correspond to an error of 0·2 c.c. in the titration value at equilibrium, *i.e.*, it is entirely negligible.

sec.-Butyl alcohol at 80·3° ($a = 1·15$, $b = 0·485$, $c = 5·22$, $K = 18·3$).

t (mins.)	0	20	40	60	60	80	120	150	260	380	480	Rise of
$N/10$-NaOH, c.c.	23·17	20·11	18·62	18·07	17·86	17·10	16·33	16·20	16·09*	16·22	16·38	0·0014 c.c. per min.

*iso*Propyl alcohol at 80·0° ($a = 1·17$, $b = 0·505$).

t (mins.)	0	630	930	1200	1560	1920	Rise of 0·0011 c.c.
$N/10$-NaOH, c.c.	23·45	16·80 *	17·10	17·35	17·90	18·30	per min.

* Minimum.

When, on the other hand, the corresponding bromides were heated at 92° with similar mixtures of phenol and aqueous hydrobromic acid, no even approximately steady state was reached. With these two bromides, the acid liberated owing to hydrolysis up to the equilibrium point should have been equivalent to 2·0 and 2·5 c.c. respectively for *sec.*-butyl and *iso*propyl bromides : with the former after 1140 mins. the increase of acid was equivalent to 4·0 c.c., and with the latter after 500 mins., 2·45 c.c.

The reaction is too slow in the absence of a catalyst for the isolation of the product, but this was achieved when phenol (50 g.) was heated with *sec.*-butyl bromide (15 g.) and a little zinc chloride at 100° until evolution of hydrogen bromide had abated (¼ hr.). The product was washed with water, dried, and distilled. The fraction of b. p. 230—242° (uncorr.) was an oil, and presumably a mixture of *sec.*-butylphenols. From it, p-sec.-*butylphenyl* p-*nitrobenzoate* was isolated in small colourless plates from light petroleum, m. p. 70° (Found : C, 68·1; H, 5·7. $C_{17}H_{17}O_4N$ requires C, 68·2; 5·7%).

Special direct tests show that no appreciable error due to nuclear condensation occurs with the alcohol SPh·[CH$_2$]$_2$·OH and its oxygen analogue.

(2) *Formation of ethers from halides and alcohols.* It is well known that triphenylmethyl bromide reacts with alcohols to yield ethers. With ethylene chlorohydrin, *triphenylmethyl* β-*chloroethyl ether* is produced, a white crystalline solid, m. p. 132° (Found : C, 78·4; H, 5·9.

$C_{21}H_{19}OCl$ requires C, 78·1; H, 5·9%). The analogous product from *tert.*-butyl bromide decomposed on distillation.

*iso*Propyl bromide (50 g.), *n*-butyl alcohol (25 g.), and phenol (100 g.) were heated together at 100° for 10 hrs. The mixture was distilled, and the portion distilling up to 150° was benzoylated in presence of pyridine over-night, recovered, and redistilled with an efficient column. Less than 0·1 g. of liquid, b. p. *ca.* 110°, was found; 45 g. of *iso*propyl bromide were recovered.

(3) *Possible hydrolysis of chlorohydrins.* It appeared possible that these compounds might undergo a further subsidiary reaction, being hydrolysed to the glycol, but in the solvent and at the temperature used, no such reaction could be detected in 6 hrs.

THE UNIVERSITY, SHEFFIELD.   [*Received, December 10th*, 1934.]

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31. *The Interaction of Alkyl Iodides and Sodium* m-4-*Xylyloxide in Ethyl Alcohol.*

By PERCY J. HARDWICK.

In various investigations on the relative reactivities of the alkyl iodides with sodium alkoxides and phenoxides, it has been necessary to compare measurements of the reaction velocity at the same dilution, since the bimolecular constants vary with the initial concentration of the reactants. Acree and co-workers (J., 1914, **105**, 2582) attributed this to simultaneous reactions of the alkyl iodide with anions and un-ionised molecules of the electrolyte and, *e.g.*, for sodium phenoxide, they calculated separate constants (k_i and k_m respectively), independent of the dilution, from the equation $k = \alpha k_i + (1 - \alpha)k_m$, where k is the observed bimolecular coefficient and α the degree of dissociation.

The object of the present work was to extend the measurements to sodium *m*-4-xylyloxide at different temperatures, and thence to calculate the heats of activation. The results indicate that, in each reaction, the measured velocity depends almost entirely on the interaction of the alkyl iodide and xylyloxide ions, negligibly small values of k_m being derived from the above relation for dual catalysis.

EXPERIMENTAL.

Preparation of Materials.—The alkyl iodides (methyl, ethyl, *n*- and *iso*-propyl, *n*- and *iso*-butyl, and *n*-amyl), supplied by Messrs. B.D.H., were washed with dilute alkali and water, dried, and fractionally distilled shortly before use. Absolute alcohol was refluxed over freshly-burnt lime, fractionated, and kept in a dry atmosphere. Sodium *m*-4-xylyloxide was prepared in alcoholic solution from equivalent amounts of sodium ethoxide and the phenol (Kahlbaum).

Course of the Reactions.—Preliminary experiments, in which equimolecular quantities of methyl iodide (14·2 g.) and the sodium salt were allowed to react to completion in dry alcohol at 25°, afforded a 92% yield of the methyl ether after it had been salted out, extracted with light petroleum, and distilled (b. p. 192—194°).

Measurement of Reaction Velocity.—Equivalent solutions of the reactants were mixed and equal quantities (10 ml.) transferred to Jena-glass tubes which were stoppered and placed in a thermostat controlled to ± 0·05°. On attaining constant temperature, a tube was withdrawn, emptied into cold water, and the residual sodium *m*-4-xylyloxide determined by titration with hydrochloric acid, the procedure being carefully standardised to avoid indicator (azolitmin) errors. This was taken as the zero of similar measurements made after suitable intervals, and the bimolecular constant was calculated from the equation $k = (1/c_t - 1/c_0)/t$, where c_0 and c_t are the concentrations (g.-mols./l.) of xylyloxide at zero time and t mins. Values of k for each reaction were determined at two temperatures for initial concentrations ranging from 0·5 to 0·05N, some 70 series of measurements being made.

In Table I some typical results for three experiments are set out in detail, the remainder being summarised in Table II, where the velocity constant for each reaction is shown to increase progressively with the initial dilution. The corresponding degree of ionisation (α) of the sodium salt, also given, was determined as described below.

TABLE I.

Methyl iodide.			Ethyl iodide.			n-Propyl iodide.		
Initial concn. = 0·493N.			Initial concn. = 0·192N.			Initial concn. = 0·0948N.		
Temp. 28·15°. HCl, 0·1733N.			Temp. 53·80°. HCl, 0·0818N.			Temp. 63·00°. HCl, 0·0380N.		
t.	Titre (ml.).	100k.	t.	Titre (ml.).	100k.	t.	Titre (ml.).	100k.
0	22·79	—	0	18·53	—	0	21·00	—
15	20·21	2·15	10	16·25	9·28	10	19·16	12·0
30	18·14	2·16	20	14·49	9·21	20	17·46	12·7
40	16·97	2·17	30	13·00	9·35	35	15·58	12·5
55	15·63	2·11	40	11·88	9·23	55	13·65	12·3
70	14·46	2·08	50	10·93	9·18	65	12·80	12·4
Mean k = 2·13 × 10⁻².			Mean k = 9·25 × 10⁻².			Mean k = 12·4 × 10⁻².		

TABLE II.

Methyl iodide.

Temp. 28·15°			Temp. 37·90°		
Initial concn., N.	α.	100k (mean).	Initial concn., N.	α.	100k (mean).
0·493	0·151	2·13	0·488	0·151	5·93
0·247	0·209	2·59	0·244	0·208	7·80
0·197	0·229	2·87	0·195	0·227	8·47
0·123	0·273	3·52	0·122	0·269	9·88
0·0986	0·296	3·83	0·0976	0·293	10·6

Ethyl iodide.

Temp. 45·40°			Temp. 53·80°		
Initial concn., N.	α.	100k (mean).	Initial concn., N.	α.	100k (mean).
0·484	0·151	2·90	0·479	0·151	6·94
0·242	0·207	3·83	0·240	0·207	8·64
0·194	0·226	4·20	0·192	0·226	9·25
0·161	0·242	4·54	0·120	0·266	10·9
0·121	0·267	5·04	0·0958	0·289	11·7
0·0968	0·291	5·44			
0·0484	0·358	7·0			

n-Propyl iodide.

Temp. 53·80°			Temp. 63·00°		
0·479	0·151	2·98	0·474	0·151	7·2
0·240	0·207	3·63	0·284	0·190	8·37
0·192	0·226	3·92	0·142	0·249	10·6
0·0958	0·289	4·86	0·0948	0·287	12·4
0·0479	0·356	6·50	0·0474	0·354	19·1

isoPropyl iodide.

Temp. 58·10°			Temp. 65·92°		
0·286	0·189	3·12	0·283	0·189	7·09
0·238	0·206	3·36	0·189	0·224	8·26
0·119	0·265	4·30	0·142	0·248	9·17
0·0953	0·287	4·62	0·0944	0·287	10·5
0·0477	0·355	6·0	0·0472	0·353	14·4

n-Butyl iodide.

Temp. 50·00°			Temp. 59·10°		
0·289	0·190	2·03	0·286	0·189	5·11
0·192	0·225	2·29	0·190	0·225	5·95
0·144	0·249	2·46	0·143	0·248	6·47
0·0962	0·289	2·83	0·0952	0·287	7·48

isoButyl iodide.

Temp. 54·00°			Temp. 65·00°;		
0·287	0·190	1·33	0·284	0·189	3·90
0·192	0·226	1·71	0·189	0·224	4·71
0·144	0·250	2·00	0·142	0·247	5·66
0·0958	0·289	2·37	0·0945	0·286	7·56

n-Amyl iodide.

Temp. 56·00°			Temp. 65·00°		
0·287	0·190	3·69	0·143	0·248	4·62	0·284	0·189	8·80	0·142	0·247	10·7
0·191	0·224	4·14	0·0955	0·289	5·35	0·189	0·224	9·80	0·0945	0·286	12·5

Determination of the Degree of Ionisation of Sodium m-4-*Xylyloxide in Alcohol.*—Conductivity measurements were made at 25° and 35°, solutions being prepared by the successive dilution of a 0·5N-solution of the sodium salt with dry alcohol containing 5% of m-4-xylenol to counteract alcoholysis. The results are summarised in Table III, where κ is the specific conductivity of the solvent in reciprocal ohms, v the dilution in l./g.-equiv., and Λ_v the corresponding equivalent conductivity, the value at infinite dilution (Λ_∞) being derived by extrapolating the straight line obtained on plotting Λ_v against $\sqrt{1/v}$ for the lowest concentrations. The degree of ionisation ($\alpha = \Lambda_v/\Lambda_\infty$) at dilutions from 2 to 32 l. was determined for other temperatures (T) from values of the equivalent conductivity (Λ_T) calculated from the equation $\Lambda_T = \Lambda_{T_0}(1 + aT)$, where Λ_{T_0} is the value at 0° and a the temperature coefficient ascertained from the given data.

TABLE III.

Temp. 25·00°.   κ = 0·32 × 10⁻⁶.

v	2	4	8	16	32	64	128	256	512	1024	2048	4096	∞
Λ_v	5·595	7·74	10·12	12·72	15·78	18·94	22·21	25·29	27·88	30·50	32·61	34·02	37·1

Temp. 35·00°.   κ = 0·24 × 10⁻⁶.

v	2	4	8	16	32	64	128	256	512	1024	2048	4096	∞
Λ_v	6·475	8·89	11·54	14·54	17·86	21·69	25·91	29·55	32·75	35·62	37·84	39·55	43·1

DISCUSSION OF RESULTS.

Values of k_i *and* k_m.—On plotting values of the velocity constant (k) at different dilutions against the degree of ionisation (α) of the sodium salt (Table II), the points obtained for each iodide lie approximately on a straight line. The data may therefore be interpreted in terms of the dual hypothesis (see p. 141). In Table IV the separate constants have been calculated from values of k and α for each pair of dilutions, the results obtained for ethyl iodide at 45·40° being recorded in detail as typical of those averaged for the other iodides.

TABLE IV.

Ethyl iodide. Temp. 45·40°.				Iodide.	Temp.	k_i (mean).	k_m (mean).	$k_i(=k/a)$ (mean).
Concns., N.	k_i.	k_m.						
0·242—0·194	0·193	−0·002		Methyl	28·15°	0·141	−0·005	0·127
0·242—0·161	0·201	−0·004			37·90	0·341	+0·009	0·370
0·242—0·121	0·198	−0·003		Ethyl..........	45·40	0·194	−0·002	0·187
0·242—0·097	0·191	−0·002			53·80	0·375	+0·011	0·410
0·194—0·161	0·210	−0·007		*n*-Propyl	53·80	0·155	+0·005	0·174
0·194—0·121	0·200	−0·004			63·00	0·371	+0·016	0·432
0·194—0·097	0·191	−0·001		*iso*Propyl	58·10	0·159	+0·001	0·163
0·161—0·121	0·194	−0·002			65·92	0·360	+0·003	0·370
0·161—0·097	0·185	+0·001		*n*-Butyl	50·00	0·084	+0·005	0·102
0·121—0·097	0·175	+0·005			59·10	0·246	+0·005	0·264
Means	0·194	−0·002		*iso*Butyl	54·00	0·101	−0·007	0·077
					65·00	0·340	−0·036	0·227
				n-Amyl	56·00	0·175	+0·003	0·188
					65·00	0·393	+0·013	0·443

In each reaction k_m is zero within the limits of experimental error. Moreover k_i, although almost independent of the dilution, is more nearly constant if calculated from the equation $k_i = k/\alpha$. This is shown by the following results for ethyl iodide at 45·40°, similarly concordant values being averaged for the other iodides in the last column of the above table.

Concn., N	....	0·484	0·242	0·194	0·161	0·121	0·097	
$k_i = k/\alpha$	....	0·192	0·185	0·186	0·188	0·189	0·187	Mean 0·187

Heats of Activation, and the Relative Reactivities of the Alkyl Iodides.—In the following table the heats of activation (E, in kg.-cals./g.-mol.) have been determined from the temperature coefficients of $k_i(= k/\alpha)$ in the usual manner. The relative reactivities, r, calculated to *n*-propyl iodide ($k_i = 10\cdot0$) at 50° as standard, are in general agreement with values found by Segaller (J., 1913, **103**, 1154) using a constant initial concentration of sodium phenoxide.

Iodide.	E.	r.	Iodide.	E.	r.
Methyl	20·5	108	*n*-Butyl	22·4	8·8
Ethyl	19·5	24·5	*iso*Butyl	21·7	4·3
n-Propyl	21·7	(10·0)	*n*-Amyl	21·2	8·6
*iso*Propyl	23·4	5·7			

The Molecular Statistics of the Reactions.—Expressed in terms of the collision theory, the velocity constant for a bimolecular reaction is given by

$$ k = \frac{N_0}{1000} \cdot \sigma_{1,2}{}^2 \left[8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{\frac{1}{2}} \cdot e^{-E/RT} $$

where M_1 and M_2 are the molecular weights of the reactants, $\sigma_{1,2}$ is the sum of their molecular radii, and N_0 the Avogadro constant, the units of k being g.-mols./l./sec.

In the reaction of ethyl iodide and *m*-4-xylyloxide ions at 45·4°, for example, $\sigma_{1,2} = 5 \times 10^{-8}$ cm. approx., $M_1 = 156$, $M_2 = 121$, and $E = 19,500$ calories; whence $k_i = 6\cdot04 \times 10^{-3}$, which is of the same order as the value $3\cdot12 \times 10^{-3}$ found experimentally, after conversion of time to seconds. The reaction may thus be classed with others involving an ion (cf. Moelwyn-Hughes, *Chem. Reviews*, 1932, **10**, 241) which usually proceed at a rate comparable with the calculated rate of activation, as distinct from the interactions of neutral molecules for which the observed velocity is frequently several powers of ten smaller than the predicted value.

SUMMARY.

The bimolecular constants (k) for the reactions of alkyl iodides with sodium m-4-xylyloxide in ethyl alcohol increase with decreasing initial concentration of the reactants.

Measurements of the degree of dissociation (α) of the xylyloxide indicate that the observed velocities are due almost entirely to the xylyloxide ions, satisfactory constants (k_i), independent of the dilution, being derived from the equation $k = \alpha k_i$.

The reactivities of the n-alkyl iodides progressively decrease to a limiting value with increasing molecular weight.

The reactions proceed at a velocity comparable with that predicted by the theory of simple collisional activation.

32. *The Catalytic Effect of Hydrogen on the Carbon Monoxide Flame.*

By W. E. GARNER and F. H. POLLARD.

THE recent advances in our knowledge of the kinetics of the *isothermal reactions* between hydrogen and oxygen at the ignition temperature, due chiefly to the researches of Hinshelwood and Semenoff, make it possible to interpret some of the phenomena observed in flames where the conditions are far from isothermal. It is the object of this paper to offer an interpretation of the action of hydrogen on the emission of radiation from the carbon monoxide flame (cf. Garner and Johnson, J., 1928, 281; Garner and Roffey, J., 1929, 1123; Garner and Hall, J., 1930, 2039; Garner, Hall, and Harvey, J., 1931, 641; Bawn and Garner, J., 1932, 129). It has been shown in the above investigations that a step or discontinuity occurs on the radiation–pressure curves of carbon monoxide flames containing hydrogen, which lies at higher pressures the smaller the concentration of hydrogen (Table I). There can be but little doubt that a change in the mechanism of the flame occurs in the neighbourhood of the step, and there are obviously two methods by which such a change of mechanism could be brought about. Either (*a*) the step represents a lower limit for the propagation of a hydrogen flame in a carbon monoxide mixture, or (*b*) it is the pressure at which two mechanisms produce flames that travel with equal speeds. The first hypothesis would provide a ready explanation of the abruptness with which the second mechanism sets in, but it is not in agreement with the fact that there is no appreciable difference between the speeds of the flame above and below the step (cf. J., 1929, 1128; 1930, 2038). On this account, hypothesis (*b*) is to be preferred.

It is well known that in order to initiate a stable flame in cold gases it is necessary to transmit to the combustible mixture, by means of a spark or hot wire, an amount of energy exceeding a minimum value which depends on the nature of the mixture, its pressure, mode of confinement, etc. This must mean that stable flames can be initiated only if a sufficient number of reaction chains are introduced into the gas. Radical or energy chains in combustible gases, such as those under review, do not reach an infinite chain length at room temperatures. Therefore, it is essential that the number of chains penetrating the cold gases ahead of the flame be sufficient to raise the temperature of these gases to that at which the chains become infinite in length, *i.e.*, to raise the temperature to the ignition temperature; if there be two independent mechanisms, then that will be dominant in flame propagation which can achieve this effect in the shortest time.

From Table I it will be seen that the pressure at which the step, p_s, occurs is given by the equation

$$(p_s \cdot p_{\text{H}_2} + 0\cdot018p_s)/3\cdot28 = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

TABLE I.

$p_{\text{H}_2} \times 10^2$, cm.	2·36	3·46	5·04	7·2	12·4	24·0
p_m, cm.	75	64·5	50	36	24	12
$p_s(p_{\text{H}_2} + 1·8 \times 10^{-2})$	3·12	3·39	3·42	3·24	3·41	3·10

For the interpretation of this equation, there are three relevant experimental observations, *viz.*, (*a*) p_s is not affected by changes in the diameter of the tube between 1·5 and 6·5 cm. (J., 1931, 642, 643), (*b*) the dilution of the combustible mixture with 33% of either oxygen or carbon monoxide has no appreciable effect on p_s (*ibid.*, p. 649), and (*c*) the addition of carbon dioxide raises the step (J., 1932, 136). The first of these observations shows that in tubes of the specified diameters there is no appreciable wall effect, and therefore de-activation of possible chain carriers by the walls can be left out of account. The second observation shows that if equation (1) is to be used to indicate a chemical mechanism, p_s cannot refer either to the pressure of oxygen or carbon monoxide or to the total pressure of the gaseous mixture. It must refer to the pressure of the combustible gas or to some product of the flame which is proportional to it. This suggests that it is the pressure of the newly-formed carbon dioxide which is one of the factors determining the step, and an obvious relationship which fits the experimental results is

$$dx_2/dt = (p_{\text{CO}_2}^* p_{\text{H}_2}/k_2 + p_{\text{CO}_2}^* k_1/k_2) \cdot dx_1/dt \quad . \quad . \quad . \quad . \quad (2)$$

where dx_1/dt and dx_2/dt are the rates of penetration of the cold gases in front of the flame by the chain carriers of the first and the second mechanism (I and II) respectively. I and II refer to the mechanisms stable at low and at high pressures respectively. The second term in equation (2) is important only at low hydrogen pressures, so that above 0·1 cm. of hydrogen, the experimental results accord with

$$dx_2/dt = (p_{\text{CO}_2}^* p_{\text{H}_2}/k_2) \cdot dx_1/dt \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

i.e., the ratios of the speeds of the two mechanisms are proportional to $p_{\text{CO}_2}^* p_{\text{H}_2}$. This can be interpreted as meaning that the first process in mechanism II is the formation of hydrogen atoms by collision of hydrogen molecules with newly formed carbon dioxide molecules,

$$\text{CO}_2^* + \text{H}_2 \longrightarrow \text{CO}_2 + 2\text{H} \quad . \quad . \quad . \quad . \quad . \quad (3a)$$
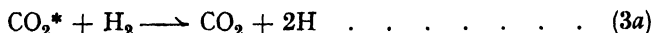
The second term in equation (2), however, indicates that there is another process which is effective at low hydrogen pressures in mechanism II. There is much uncertainty as to what this term can mean, since in such complicated processes a term of this sort can have many meanings. A possible interpretation is that it refers to a second type of re-action chain, and that mechanism II is composite in character. If this be accepted as the correct explanation, then the two simultaneous processes of mechanism II can be written as in (3*b*) and (3*c*) :

$$\text{CO}_2^* + \text{H}_2 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}_2 \quad . \quad . \quad . \quad . \quad (3b)$$
$$\text{H}_2\text{O}_2 \longrightarrow 2\text{OH}$$
$$\text{OH} + \text{CO} \longrightarrow \text{CO}_2 + \text{H}$$
$$\text{CO}_2^* + \text{O}_2 \longrightarrow \text{CO}_2 + 2\text{O} \quad . \quad . \quad . \quad . \quad . \quad (3c)$$
$$\text{O} + \text{CO} + \text{M} \longrightarrow \text{CO}_2^* + \text{M}$$
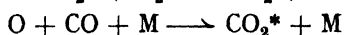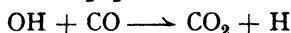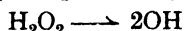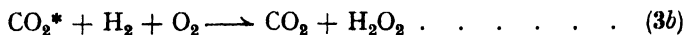
These two processes are interlinked, for atomic oxygen can be produced in the reactions of atomic hydrogen and *vice versa*, so that (3*a*) and (3*b*) give two ways of setting into train one mechanism of reaction. Thus, on this view, hydrogen atoms are the carriers mainly responsible for the forward movement of mechanism II : this would be expected on account of their very high mobility.

There is very little information throwing light on the kinetics of mechanism I, except that the velocity of the flame at atmospheric pressure increases linearly with increase in the hydrogen pressure (J., 1930, 2039) ; it is only possible at present to describe its speed in terms of equation (2).

The principal conclusion to be drawn from the above results is that the rate of production of hydrogen atoms is proportional to $p_{CO_2}.p_{H_2} + 0.018p_{CO_2}$, and that the position of the step is mainly determined by the density of the hydrogen atoms penetrating the cold gases ahead of the flame. The hydrogen mechanism takes control of the flame when the density of these atoms in the flame front exceeds a minimal value; this value must increase with increase in pressure of the combustible gases, and also with increase in the hydrogen pressure, since the rate of mechanism I increases in this way.

The breaking of the reaction chains normally occurs on the walls or by collision of two chain carriers, *e.g.*, by $H + H + M \longrightarrow H_2 + M$ and $H + OH + M \longrightarrow H_2O + M$. The first of these processes is not very important in vessels of 2·0 cm. diameter and at gas pressures exceeding 20 cm., and the latter is probably of little importance in the propagation of flame since the hydrogen pressures are small. The extinguishing effect of carbon dioxide on flames is well known, so that this gas, at least in an unactivated state, probably can break the hydrogen chain.

The Action of Carbon Dioxide on the Flame.—On diluting the combustible mixture with carbon dioxide, the pressure of the hydrogen required to make the hydrogen mechanism dominant is increased (Table II). This is in contrast with the effect obtained on dilution with 33% of oxygen or carbon monoxide, which does not change the position of the step. It follows, therefore, that if excess of carbon monoxide and oxygen affects the speeds of the two mechanisms, either by their entering into the reaction or by their presence as inert gases, they must change both to the same degree. The effect produced by carbon dioxide is evidently specific to the chemical nature of this gas.

The reduction in efficiency of the hydrogen by carbon dioxide is given by the equation

$$p_{H_2} - p_{H_2}' = \text{const.} \times p_{CO_2}. \quad \quad \quad \quad (4)$$

where p_{H_2} is the pressure of the hydrogen at p_s, and p_{H_2}' is that required to produce a step at p_s in the absence of carbon dioxide. The latter is calculated from equation (1). The values are given in Table II (where pressures are in cm.), and it will be seen that $(p_{H_2} - p_{H_2}')/p_{CO_2} = 6.9 \times 10^{-3}$ within the error of measuring the step. Hence, the pressure of the step in the presence of carbon dioxide is given by the empirical equation

$$p_s p_{H_2} + (1.8 \times 10^{-2})p_s = 3.49 + 6.9 \times 10^{-3}p_s p_{CO_2} \quad \quad \cdot \quad (5)$$

TABLE II.

p_s.	p_{CO_2}.	$100p_{H_2}$.	$100p_{H_2}'$.	$\dfrac{p_{H_2}-p_{H_2}'}{p_{CO_2}} \times 10^3$.	p_s.	p_{CO_2}.	$100p_{H_2}$.	$100p_{H_2}'$.	$\dfrac{p_{H_2}-p_{H_2}'}{p_{CO_2}} \times 10^3$.
33	0·0	8·77	—	—	43·5	7·91	11·58	6·23	6·8
38	3·80	10·1	7·40	7·1	54·5	13·62	14·50	4·61	7·3
40	5·72	10·63	6·92	6·5					Average 6·9

The figures in col. 4 are calculated from the equation $p_{H_2}' = (3.49 - 0.018p_s)/p_s$, thus making a small allowance for the fact that the step occurs at a slightly higher pressure in the quartz bomb used in the measurements than in the metal bomb used by Hall. This seems to be the most reasonable way of making the correction, which, however, makes little difference to the results in col. 5.

It is suggested that the molecules of carbon dioxide break the reaction chains of mechanism II, thereby diminishing the density of the stream of hydrogen atoms. This stream has a density at the step which is proportional to $p_s p_{H_2} + 0.018p_s = 3.49$, and this, according to the theory of chain reactions, will be reduced in the presence of carbon dioxide by the factor $k_1 p_x^n/(k_1 p_x^n + k_2 p_y^m p_{CO_2})$, where $k_1 p_x^n$ refers to the velocity of the process whereby the chains are carried on, and $k_2 p_y^m p_{CO_2}$ refers to the process of breaking the chains. Equation (5) can be derived from this if $p_x^n = 1$ and $p_y^m = p_s$. On making these assumptions, the density of the hydrogen-atom stream in the presence of carbon dioxide becomes proportional to $p_s(p_{H_2} + 0.018)k_1/(k_1 + k_2 p_{CO_2} p_s)$, and, providing that there be no other effects of carbon dioxide on the flame than those common to both mechanisms, the pressure of the hydrogen at the step will be given by the equation $p_s(p_{H_2} + 0.018) = 3.49 + p_{CO_2} p_s k_2/k_1$, which is in accord with that found experimentally.

The action of carbon dioxide can thus be quantitatively interpreted as due to that of breaking the hydrogen chains. It is suggested that the chains are broken by the collisions of hydrogen peroxide molecules with carbon dioxide to give percarbonic acid,
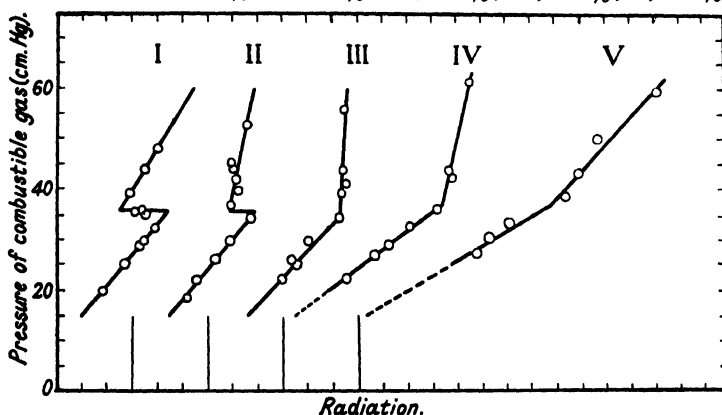
$$H_2O_2^* + CO_2 + M \longrightarrow CO_2(OH)_2 + M, \quad \ldots \ldots (6a)$$
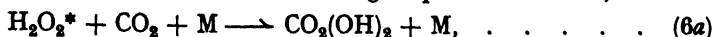
and the chain is carried on by

$$H_2O_2^* \longrightarrow 2OH \quad \ldots \ldots \ldots (6b)$$

Provided that the breaking of the chains by carbon dioxide occur much more frequently than by any other similar process, this mechanism is in accord with the facts presented in equation (5).

FIG. 1.

Chlorine contents : I, 0% ; II, 1·01% ; III, 2·01% ; IV, 2·95% ; V, 3·93%.

The Action of Halogens on the Flame.—Since the halogens combine with hydrogen atoms, it would be expected that they would exert an appreciable effect on the pressure at which the step occurs. It has been found that both chlorine and bromine do, in fact, caused marked changes in the pressure–radiation diagrams of the equimolecular mixture containing 0·02% hydrogen. Chlorine, however (Fig. 1), has only a slight effect on the position of the step, and therefore affects mechanisms I and II almost equally; it diminishes the speed of the flame, and 4—5% of chlorine causes its extinction. Bromine, on the other hand (Fig. 2), gives a series of diagrams which resemble those obtained with carbon dioxide, the step being raised from 35·5 to 48·5 cm. by the addition of 4% of bromine. As with chlorine, 4—5% of bromine extinguishes this flame.

A marked difference between the action of the two gases is shown in the amounts of radiation emitted above the step. As the chlorine per-

FIG. 2.

Bromine contents: I, 0% ; II, 0·98% ; III, 2·02% ; IV, 3·92%.

centage increases, the step gradually disappears owing to the fact that the radiation emitted during mechanism II becomes similar in magnitude to that emitted during mechanism I. No such effect is observed with bromine. The radiation is emitted from the gaseous products and its magnitude decreases as the percentage of water increases. Therefore the action of chlorine is probably due to the drying of the gaseous products by the reaction

$$2H_2O + 2X_2 \longrightarrow 4HX + O_2 \quad \ldots \ldots \ldots (7)$$

At the temperature of the flame, this reaction occurs to a greater extent with chlorine than with bromine. A discussion of the radiation phenomena now would tend to confuse the issue, and so is postponed.

The interaction of hydrogen atoms with halogen molecules, which occurs according to the scheme

$$H + X_2 \longrightarrow HX + X \quad (8a); \quad X + H_2 \longrightarrow HX + H \quad . \quad . \quad . \quad (8b)$$

has different consequences in the case of the two halogens; (8b), although occurring readily in the case of chlorine, possesses a high critical increment in that of bromine, so chlorine atoms possess a shorter life than bromine atoms. Polanyi (*Trans. Faraday Soc.*, 1928, **24, 606**) found that bromine was an effective breaker of the chain for the reaction between hydrogen and chlorine. Consequently, bromine is likely to be much more effective than chlorine in reducing the density of the hydrogen chains in mechanism II and therefore should be more effective in raising the step, and this is, in fact, found :

Added gas (Cl_2 or Br_2), %	0	1	2	3	4
p_s, cm., for added Cl_2	35·5	35·5	35·5	37·5	—
p_s, cm., ,, Br_2	35·5	38·0	41·3	—	48·5

The action of bromine can be represented by an equation similar to that found for carbon dioxide, *viz.*,

$$p_s(p_{H_2} + 0.018) = 3.16 + 2.8 \times 10^2 p_{Br_2} p_s. \quad . \quad . \quad . \quad . \quad (9)$$

as will be seen from Table III (pressures in cm.). The errors in measuring the step are, however, so large that the measure of agreement found in col. 5 is better than corresponds to the experimental error. This means that the pressure of hydrogen at the step is raised

TABLE III.

p_s.	p_{Br_2}.	p_{H_2}.	p_{H_2}'.	$(p_{H_2}-p_{H_2}')/p_{Br_2}$.	p_s.	p_{Br_2}.	p_{H_2}.	p_{H_2}'.	$(p_{H_2}-p_{H_2}')/p_{Br_2}$.
35·5	0·0	0·071	—	- -	41·3	0·834	0·0825	0·058	0·029
38·0	0·372	0·076	0·065	0·029	48·5	1·900	0·097	0·047	0·026
									Mean 0·028

by the factor $(k_1 + k_2 p_{Br_2} p_s)/k_1$, which indicates that the chains are broken by bromine in a similar manner to that suggested for carbon dioxide. It does not appear that the bromine molecules break the hydrogen chains by collision with hydrogen atoms, for this process requires a very different factor. The chains are probably broken in a termolecular collision with a chain carrier which otherwise decomposes spontaneously. Such chain carriers are HO_2 and H_2O_2, but as there have been no experimental studies of the reactions of such radicals with bromine, it is unprofitable to discuss the action of bromine any further at this stage.

The Percentage Combustion of the Gases.—The mixture of combustible gases containing 0·02% of hydrogen undergoes 90—95% combustion in a quartz vessel 2 cm. in diameter. As can be seen from a visual examination of the slow flames, there is a skin of unburnt gases in the neighbourhood of the walls, and this owes its existence to loss of heat from the flame and to the breaking of reaction chains on the walls. That it is very largely due to the latter cause, is shown by the fact that excess oxygen or carbon monoxide in the flame is particularly active in reducing the thickness of this skin of cold gas. When 33% excess of carbon monoxide is added, the combustion is practically complete (J., 1931, 651). This wall effect, although reducing the percentage combustion, does not affect the position of the step.

When either chlorine or bromine is added to the combustible mixture, the percentage combustion shows a minimum in the neighbourhood of the step (Fig. 3). This shows that the walls exert a greater influence on the chains of mechanism II than on those of mechanism I. This confirms the conclusions reached previously. The carrier for mechanism II, which is broken on the walls, may be a halogen atom, but this is unlikely since similar results are obtained for both halogens. It is very probable that the carriers are hydrogen atoms which, on account of their high mobility, are particularly liable to be removed by
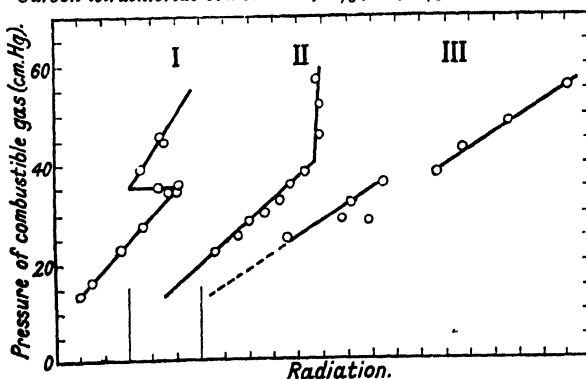
the walls.* The minimum on the percentage combustion curve is not found in the combustible gases in the absence of the halogens, probably because the velocity of the flame is too high. When the speed of flame is reduced by the addition of halogens, the wall effect can then appear. The percentage combustion commences to fall within the region of mechanism I, *i.e.*, below 36 cm. This would be expected from the experiments of Roffey on the ionisation of the flame, which showed that below the step there were two successive waves of ionisation (J., 1929, 1135), which were interpreted as indicating that in this region the two reaction mechanisms are successive.

The Effect of Carbon Tetrachloride.—Earlier measurements (J., 1928, 288) had given qualitative indications of the marked effects of this substance on the radiation emitted from the hydrogen-containing flames. In the present research, it is found that carbon tetrachloride has a greater effect than chlorine as a breaker of the reaction chains of mechanism II, 1% raising the step from 35·5 to 39·5 cm. (Fig. 4). The interaction of carbon tetrachloride with hydrogen atoms could result in the breaking of the hydrogen chains by the reaction $CCl_4 + H = CCl_3 + HCl$ (cf. Polanyi, "Atomic Reactions," 1932, for similar processes).

In one respect carbon tetrachloride differs from bromine and chlorine : although it markedly reduces the percentage combustion, it does not show a minimum at the step. A possible explanation of this is that the vapour is adsorbed on the walls to give a multimolecular layer which returns some of the hydrogen atoms to the gas unchanged. In Fig. 4, curve III, the step appears to be reversed, but this is because the flame in the lower region of pressure did not reach the end of the tube.

FIG. 3.

Chlorine contents : I, 0%; II, 1·01%; III, 2·01%; IV, 2·95%; V, 3·98%.

Combustion, %.

Pressure of combustible gas (cm. Hg).

FIG. 4.

Carbon tetrachloride contents : I, 0%; II, 1%; III, 2·15%.

Pressure of combustible gas (cm. Hg).

Radiation.

EXPERIMENTAL.

The apparatus employed and the experimental procedure were similar to that described in previous papers. The flames were produced in the quartz vessel previously used by Bawn.

* Bradford's results (J., 1933, 1557) on the composition of the gases after explosion of mixtures of carbon monoxide, hydrogen, and oxygen can be explained on the same basis.

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Chlorine, bromine, or carbon tetrachloride vapour was introduced into the quartz vessel by breaking a glass bulb by a magnetically-released plunger. The tap leading to the quartz tube was closed after allowing 2 mins. for the gas to be evenly distributed, and then the tubes and breaker were re-evacuated. Care had to be taken to prevent contamination of chlorine, etc., with the pump oil and the mercury in the manometers and mercury-vapour pump. Dry air was first admitted to the tubes, etc., and then pumped out by means of an efficient water-pump. More dry air was then admitted, pumped out with the water-pump, and finally completely evacuated with the Hyvac and the mercury pump in series. When a good vacuum had been obtained, the tap to the pump was closed and the carbon monoxide–oxygen–0·2% hydrogen mixture admitted until the pressure was slightly in excess of that required. The tap to the bomb was then opened, and the mixture allowed to flow into it. The pressure was then quickly adjusted to that required, and the tap to the bomb closed. In this way none of the foreign gas, *i.e.*, chlorine, etc., was able to escape back into the tubes. It was found necessary to allow 10—15 mins. for the gases in the bomb to mix before they were ignited and the radiation measured as described in the previous papers. Great care was taken to prevent chlorine attacking the tap grease; it was found satisfactory to grease the central part of the plug of the tap with the chlorine-resisting grease described by Guye (*J. Chim. physique*, 1908, **6**, 756) and Wourtzel (*ibid.*, 1913, **11**, 31), and the outer part of it with Apieson grease.

Preparation of the Bulbs of Gas.—Constrictions were made in thin-walled glass tubing so that it formed a series of bulbs. After the volume of the bulbs had been calibrated by filling with either water or mercury, they were cleaned with concentrated nitric acid, then distilled water, and finally rinsed with absolute alcohol, and dried by means of a stream of hot, dry air; 30—40 of these bulbs were then sealed on to an apparatus containing the gases to be used in an experiment.

Chlorine. The chlorine, prepared by the action of pure hydrochloric acid on Kahlbaum's potassium permanganate, was passed through solutions of potassium permanganate and copper sulphate, and dried first with concentrated sulphuric acid and then with phosphoric oxide. The bulbs were filled by displacement of air, a rapid stream of chlorine being first passed through them, then a steady stream, a rapid stream again, and finally a steady stream. They were then sealed off at calibrated marks and stored in numbered compartments. The temperature and pressure of filling were noted. All joints in the apparatus were glass to glass.

Bromine. Bromine vapour was obtained from Kahlbaum's pure liquid, which was placed in a bulb and connected through a phosphoric oxide tube to a series of calibrated bulbs. The bromine was immersed in liquid air, and the whole of the apparatus evacuated by means of a Hyvac pump. The tap to the pump was closed and the liquid air removed. When the bromine had reached a suitable temperature, it was surrounded by water contained in a Dewar flask at a temperature slightly lower than that of the room; ½ hour was then allowed for the vapour to fill the bulbs. The temperature of the liquid bromine was recorded, so that the pressure of the vapour in the bulbs could be calculated. The bulbs were then carefully sealed off and stored.

Carbon tetrachloride. A similar method was employed to fill bulbs with vapour from Kahlbaum's carbon tetrachloride.

Results.—The radiation was measured by means of a Moll microthermopile with fluorite window, and a Downing galvanometer, the deflexion of the latter being recorded on photographic paper. The area below the curve obtained is taken to be proportional to the radiation emitted, and this area is multiplied by the reciprocal of the fraction of the gas burned to give the results recorded on Figs. 1, 2, and 4. These are plotted against the pressure of the combustible gas present. This procedure was the same as that adopted in the earlier work. The pressure of the gases after the flame had passed was measured on a mercury manometer, and from these data the percentage combustion was calculated.

CONCLUSIONS.

It is shown that, in the carbon monoxide flame containing hydrogen, there are two independent mechanisms whereby flame is produced. The pressure at which the two mechanisms travel at the same speed is given by $p_s = k_2/(p_{H_2} + k_1)$. It is concluded that the velocity of the mechanism stable at the higher pressures is dependent on the rate at which hydrogen atoms are produced by collision of hydrogen molecules with newly-

formed carbon dioxide molecules. Carbon dioxide, chlorine, bromine, and carbon tetrachloride diminish the density of the stream of hydrogen atoms and raise p_s. An interpretation of the results is given in terms of the theory of chain reactions.

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33. *The Action of Titanous Chloride on Nitrophenylhydrazones :* p-*Nitro- and* 2 : 4-*Dinitro-phenylhydrazones.*

By A. KILLEN MACBETH and J. R. PRICE.

THE results of previous workers show that phenylhydrazones may be converted by the action of suitable reducing agents into a mixture of primary bases, the first stage in the reaction evidently being the formation of a symmetrically substituted hydrazine, which subsequently undergoes scission to give the final reaction products. Thus, sodium amalgam converts benzaldehydephenylhydrazone in boiling alcoholic solution into *s*-phenylbenzylhydrazine, whereas in the presence of acetic acid the hydrazone or the hydrazine is converted into benzylamine and aniline (Schlenk, *J. pr. Chem.*, 1908, **78**, 49). A similar result has been recorded for other phenylhydrazones by treatment with activated aluminium (Matzierevich, *J. Russ. Phys. Chem. Soc.*, 1925, **57**, 221) or by electrolytic reduction (Tafel and Pfeffermann, *Ber.*, 1902, **35**, 1510). Catalytic reduction by hydrogen in the presence of colloidal platinum carries the reaction on phenylhydrazones to the *s*-substituted hydrazine stage only (Goodwin and Bailey, *J. Amer. Chem. Soc.*, 1925, **47**, 167).

Since titanous salts are employed as reducing agents mainly in moderately concentrated acid media, hydrolysis of the phenylhydrazones into the constituent phenylhydrazines and carbonyl compounds is to be expected rather than reduction at the double bond of the carbon–nitrogen linkage : and this course is in fact found to be followed. As it was desired to test the suitability of titanous chloride as a quantitative reagent in the analysis of nitrophenylhydrazones, representative compounds of this type were examined. We have confirmed the fact that *p*-nitrophenylhydrazine itself is reduced by this reagent to *p*-phenylenediamine and ammonia (Robinson, *J. Manch. Sch. Tech.*, 1915, **7**, 105). In the case of 2 : 4-dinitrophenylhydrazine no such scission occurs, the reaction evidently yielding 2 : 4-diaminophenylhydrazine on a quantitative basis. The estimation of *p*-nitrophenylhydrazones must therefore be based on a consumption of eight equivalents of hydrogen (or titanous salt), and 2 : 4-dinitrophenylhydrazones on the basis of twelve such equivalents, in accordance with the following equations :

$$NO_2 \cdot C_6H_4 \cdot NH \cdot NH_2 + 8TiCl_3 + 9HCl = C_6H_4(NH_2)_2 + NH_4Cl + 8TiCl_4 + 2H_2O$$
$$(NO_2)_2C_6H_3 \cdot NH \cdot NH_2 + 12TiCl_3 + 12HCl = (NH_2)_2C_6H_3 \cdot NH \cdot NH_2 + 12TiCl_4 + 4H_2O$$
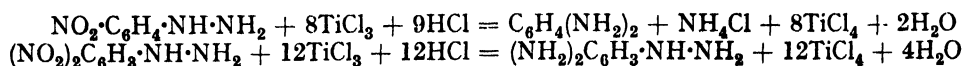
This behaviour of 2 : 4-dinitrophenylhydrazine is in agreement with the observation of Rathsburg (*Ber.*, 1921, **54**, 3183) that the nitro-groups of trinitrophenylmethylnitroamine are quantitatively reduced by titanous chloride without apparent scission of the molecule.* Phenylhydrazine and *p*-bromophenylhydrazine are unattacked by titanous salts, and so no reduction is to be expected in the case of their phenylhydrazones.

EXPERIMENTAL.

Preparation of Materials.—(a) Acetaldehydephenylhydrazone was prepared by the method of Laws and Sidgwick (J., 1911, **99**, 2085) and isolated as the β-form (m. p. 57—58°) on crystal-

* There is evidently a misprint in this paper, since reference is made to trinitrophenylnitroamine, and not to trinitrophenylmethylnitroamine. The results recorded, however, agree with the latter and not with the former, and the reference given for these substances (van Duin, *Chem. Weekblad*, 1919, **16**, 1111) deals with trinitrophenylmethylnitroamine.

lisation from an acid medium. The same method was applied in the case of acetonephenyl-hydrazone, which was converted into the hydrochloride (m. p. 143—144°, decomp.). Neither these substances nor phenylhydrazine hydrochloride was reduced by titanous chloride solution under the standard conditions of analysis (Knecht and Hibbert, *Ber.*, 1903, **36**, 1549).

(b) Terpene *p*-nitrophenylhydrazones were prepared by filtering a hot solution of *p*-nitrophenylhydrazine (1·2 g.) in *N*-hydrochloric acid (50 ml.) into an alcoholic solution (10 ml.) of the carbonyl compound (1 g.). The mixture was then poured into 30% acetic acid (100 ml.) and after some hours the product was collected and recrystallised from methyl or ethyl alcohol. The mixing with acetic acid is unnecessary in the case of the simpler aliphatic aldehydes and ketones.

(c) 2 : 4-Dinitrophenylhydrazones were prepared by Brady's method (J., 1931, 756). The m. p.'s were in agreement with those generally recorded in the literature, and the higher m. p.'s for the 2 : 4-dinitrophenylhydrazones of formaldehyde and acetaldehyde given by Bryant (*J. Amer. Chem. Soc.*, 1932, **54**, 3760) were confirmed.

Phellandral forms a p-*nitrophenylhydrazone*, yellow-orange rosettes from methyl alcohol, m. p. 169—170° (Found : C, 66·8; H, 7·4. $C_{16}H_{21}O_3N_3$ requires C, 66·9; H, 7·3%), and a 2 : 4-*dinitrophenylhydrazone*, small orange to red-orange needles from chloroform–ethyl alcohol, m. p. 202—203° (Found : C, 57·6; H, 5·7. $C_{16}H_{20}O_4N_4$ requires C, 57·8; H, 6·0%).

The following 2 : 4-*dinitrophenylhydrazones* were prepared : of diethyl ketone, orange needles from alcohol, m. p. 156° (Found : C, 49·45; H, 5·4. $C_{11}H_{14}O_4N_4$ requires C, 49·6; H, 5·3%); of *o*-chlorobenzaldehyde, orange needles from glacial acetic acid, m. p. 209° (Found : Cl, 11·1. $C_{13}H_9O_4N_4Cl$ requires Cl, 11·1%); of 4-*iso*propyl*cyclo*hexan-1-one, orange-yellow plates from alcohol, m. p. 119—120° (Found : C, 56·4; H, 6·15. $C_{15}H_{20}O_4N_4$ requires C, 56·25; H, 6·25%); of thujone, orange-yellow plates from alcohol, m. p. 116—117° (Found : N, 17·0. $C_{16}H_{20}O_4N_4$ requires N, 16·9%); of protocatechualdehyde, dark red micro-crystals from methyl alcohol, m. p. 275° (decomp.) (Found : N, 17·6. $C_{13}H_{10}O_6N_4$ requires N, 17·6%); of vanillin, orange-red micro-crystalline prisms from glacial acetic acid, m. p. 267—268° (Found : C, 50·6; H, 3·6. $C_{14}H_{12}O_6N_4$ requires C, 50·6; H, 3·6%); and of veratraldehyde, microscopic orange prisms from ethyl acetate, m. p. 264—265° (Found : C, 51·8; H, 4·1. $C_{15}H_{14}O_6N_4$ requires C, 52·0; H, 4·05%).

Analytical Results.—In the table the percentages shown in the last column were determined experimentally on the basis of the number of equivalents of titanous chloride (or titanous sulphate) shown. The standard volumetric method for the estimation of nitro-groups was employed, some 75% excess of titanous chloride being used, and the unoxidised residue being measured either by direct titration with standardised methylene-blue, or by back-titration with titanous chloride after the addition of excess of the methylene-blue. Some of the dinitrophenylhydrazones examined were too sparingly soluble for use in the estimations, and as a rule the nitrophenylhydrazones of aromatic aldehydes and ketones are of this type.

Substance.	TiCl₃, equivs.	% found.
p-Nitrophenylhydrazine	8	100·3
Acetaldehyde-*p*-nitrophenylhydrazone	8	98·3
n-Butaldehyde-*p*-nitrophenylhydrazone	8	100·0
Phellandral-*p*-nitrophenylhydrazone	8	100·3
l-4-*iso*Propyl-Δ²-*cyclo*hexen-1-one-*p*-nitrophenylhydrazone	8	99·0
2 : 4-Dinitrophenylhydrazine	12	100·3
Formaldehyde-2 : 4-dinitrophenylhydrazone	12	99·8
Acetaldehyde-2 : 4-dinitrophenylhydrazone	12	100·9
n-Butaldehyde-2 : 4-dinitrophenylhydrazone	12	100·0
n-Heptaldehyde-2 : 4-dinitrophenylhydrazone	12	100·0
Acetone-2 : 4-dinitrophenylhydrazone	12	100·0
Diethyl ketone-2 : 4-dinitrophenylhydrazone	12	100·2
Thujone-2 : 4-dinitrophenylhydrazone	12	99·2
4-*iso*Propyl*cyclo*hexan-1-one-2 : 4-dinitrophenylhydrazone	12	100·0
l-4-*iso*Propyl-Δ²-*cyclo*hexen-1-one-2 : 4-dinitrophenylhydrazone	12	100·2

Hydrolysis of Hydrazones.—It was thought desirable to apply a test to detect the hydrolysis of the phenylhydrazones during the titanium estimations. The carbon dioxide issuing from the reaction flask carries with it vapours of the carbonyl compounds, and if these are passed into a solution of 2 : 4-dinitrophenylhydrazine in 10% sulphuric acid, precipitates of the re-formed hydrazones are obtained, but in amounts too small to admit of identification. In a larger-scale experiment *n*-butaldehyde-2 : 4-dinitrophenylhydrazone was refluxed with 3*N*-hydrochloric acid as in the titanium estimation method, and the carbon dioxide was passed

into a sulphuric acid solution of 2 : 4-dinitrophenylhydrazine : after filtration and recrystallisation, the precipitate had m. p. 121—122°, alone or mixed with authentic *n*-butaldehyde-2 : 4-dinitrophenylhydrazone.

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34.   *The Resolution of Tertiary Hydroxy-carboxylic Acids.*

By EDWIN W. CHRISTIE, ALEX. MCKENZIE, and ALEX. RITCHIE.

THE only tertiary hydroxy-carboxylic acid to be resolved into its optically active components by means of alkaloids is *r*-atrolactinic acid, which McKenzie and Clough (J., 1910, **97**, 1016) resolved by morphine and by quinine.

For purposes of other investigations it was desired to obtain other optically active acids of the same type, OH·CRR'·CO₂H, as atrolactinic acid, but difficulties were encountered at the outset when attempts to resolve four different acids of this type met with no success. This was all the more curious when it was recalled that, in spite of the great success of Pickard and Kenyon in resolving many secondary alcohols, the only tertiary alcohol containing the hydroxyl group attached to the asymmetric carbon atom which has hitherto been resolved is α-terpineol. For the purpose of obtaining (−) and (+)terpineols Fuller and Kenyon (J., 1924, **125**, 2304) crystallised the brucine and the morphine salts of α-terpinyl hydrogen phthalate.

We have, nevertheless, prosecuted our attempts in an unpromising field, and have resolved *r*-phenyl-*p*-tolylglycollic, *r*-*p*-tolylmethylglycollic, and *r*-anisylmethylglycollic acids.

The optically active anisylmethylglycollic acids described by McKenzie and P. D. Ritchie (*Biochem. Z.*, 1932, **250**, 376) were prepared by them, not by the resolution of the *r*-acid, but by asymmetric syntheses, thus :
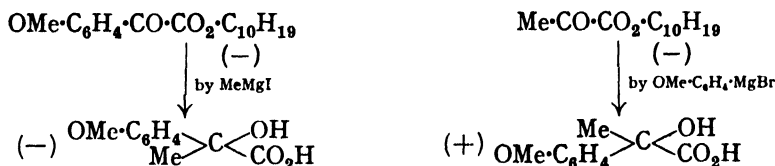
From these syntheses it was possible to isolate the two acids from the mixtures resulting from the Grignard actions by crystallising from benzene the partially active product in each case, the *r*-acid remaining in the filtrate. These are the only examples where an optically pure compound can be obtained from the product of an asymmetric synthesis when compounds of known constitution are employed. The (−)acid now obtained by resolving the *r*-acid with morphine agreed in m. p. and rotatory power with the (−)acid obtained from (−)menthyl anisoylformate.

EXPERIMENTAL.

r-4-*Methoxybenzilic acid*, prepared by the action of alcoholic potash on 4-methoxybenzil (McKenzie, Luis, Tiffeneau, and Weill, *Bull. Soc. chim.*, 1929, **45**, 414), crystallised from benzene or water in needles, m. p. 148—149° (Found : C, 69·8; H, 5·6. C₁₅H₁₄O₄ requires C, 69·7; H, 5·5%). A trace gave an orange coloration with concentrated sulphuric acid.

Attempts to resolve this acid, as well as *r*-methylethylglycollic acid, *r*-phenyl-α-naphthylglycollic acid, and *r*-benzylphenylglycollic acid by means of various alkaloids were unsuccessful, although crystalline alkaloidal salts were available in each case.

Resolution of r-*Phenyl*-p-*tolylglycollic Acid.*—Hydrated quinine (45 g.) was dissolved in a boiling solution of 34 g. of *r*-phenyl-*p*-tolylglycollic acid (McKenzie and Christie, J., 1934, 1070) in ethyl alcohol (1100 c.c.), the amount calculated for quinine trihydrate being 53 g. After 5 hours at the ordinary temperature, the bulky crystals (27 g.) were collected, and recrystallised four times from ethyl alcohol; the homogeneous quinine salt (12 g.) of the (+)acid

was then obtained as rosettes of needles. The progress of the resolution was noted by decomposing the filtrates from successive crystallisations by means of dilute sulphuric acid and determining the rotatory power of the acids so obtained. The quinine salt was acidified by dilute sulphuric acid, the organic acid being then extracted with ether.

(+)*Phenyl*-p-*tolylglycollic acid* crystallised from acetone–light petroleum (b. p. 80—100°) in long prisms, m. p. 125—127° (Found : C, 74·8; H, 6·0. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%), whereas the *r*-acid has m. p. 133—134°. A trace gave a cherry-red coloration with concentrated sulphuric acid. In ethyl alcohol : $l = 2$, $c = 5·2965$, $\alpha_{5461}^{20°} + 0·26°$, $[\alpha]_{5461}^{20°} + 2·5°$, the rotatory power being unchanged after the acid had been crystallised.

r-Phenyl-*p*-tolylglycollic acid was reduced by hydriodic acid and phosphorus in the presence of glacial acetic acid. The product was *r*-phenyl-*p*-tolylacetic acid (McKenzie and Widdows, J., 1915, **107**, 702). When (+)phenyl-*p*-tolylglycollic acid was reduced under similar conditions, the product after one crystallisation from dilute acetic acid was *r*-phenyl-*p*-tolylacetic acid, and the filtrate also was optically inactive. This observation has a bearing on Walden inversion where a compound with a hydroxyl group in direct attachment to the asymmetric carbon atom is converted into another where hydrogen is substituted for the hydroxyl group, an aspect which had not been investigated so far.

Ethyl (+)*phenyl*-p-*tolylglycollate*, prepared by esterifying the (+)acid with ethyl alcohol and sulphuric acid, was a mobile oil (Found : C, 75·6; H, 6·5. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%). In acetone : $l = 2$, $c = 4·659$, $\alpha_{5461}^{21°} + 0·41°$, $[\alpha]_{5461}^{21°} + 4·4°$. The oil was distilled under 18 mm., the fraction (b. p. 205—210°) was collected, and found to have the same rotation as that just quoted.

Action of p-Tolylmagnesium Bromide on Pyruvic Acid.—The Grignard reagent prepared from 116 g. of *p*-bromotoluene (3 mols.) was added slowly with mechanical stirring to an ethereal solution of 20 g. of freshly-distilled pyruvic acid (1 mol.). A cream-coloured bulky solid separated. After 2½ hours' heating and subsequent decomposition of the additive complex with ice and dilute sulphuric acid, the ethereal layer was removed, the ether expelled, and the product distilled in steam to remove *p*-ditolyl; the residue was extracted with ether. Under diminished pressure the resulting reddish oil solidified gradually, and the solid was crystallised twice from ethyl alcohol–light petroleum (b. p. 60—80°). Yield, 15 g.

r-p-*Tolylmethylglycollic acid* forms needles, m. p. 102—104° (Found : C, 66·6; H, 7·0. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%). A trace gave no coloration with concentrated sulphuric acid but when more was added the solution became yellow. This colour reaction is not nearly so delicate as that exhibited either by 4-methoxybenzilic acid or by phenyl-*p*-tolylglycollic acid.

Resolution of r-p-*Tolylmethylglycollic Acid.*—Hydrated quinine (28·8 g.) was dissolved in a boiling solution of the *r*-acid (15 g.) in ethyl alcohol (200 c.c.), the amount calculated for quinine trihydrate being 31·5 g. After 5 hours at the ordinary temperature, the crystals when dried under diminished pressure at 90° amounted to 28 g., and had m. p. 160—184°. These were crystallised repeatedly from ethyl alcohol : the diastereoisomeride of the (—)acid was the more sparingly soluble of the two, but the resolution was slow. The successive crops amounted to 28, 22, 15, 9·3, 5·7, 4·8, 4·3, 3·8, 3·2, and 2·3 g. respectively when dried in a vacuum at 80°, and the corresponding acids recovered from the mother-liquors gave for $[\alpha]_{5461} + 8·6°$, $+ 1·1°$, $+ 15·4°$, $+ 5·6°$, $+ 0·9°$, $- 15·3°$, $- 29·5°$, $-42·4°$, $- 47·8°$ and $- 50°$ in ethyl alcohol. The final crystals (m. p. 202—204°) of the quinine salt of the (—)acid amounted to 2·3 g., and gave after acidification with dilute sulphuric acid and extraction with ether an acid (m. p. 140—142°) with $[\alpha]_{5790}^{20°} - 43·4°$ and $[\alpha]_{5461}^{20°} - 50·6°$ ($c = 1·935$) in ethyl alcohol. This acid was recrystallised from ethyl alcohol–light petroleum (b. p. 80—100°).

(—)p-*Tolylmethylglycollic acid* separated in long prismatic needles, m. p. 140—142° (Found : C, 66·6; H, 6·9. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%). In ethyl alcohol : $l = 2$, $c = 1·5435$, $\alpha_{5790}^{20°} - 1·36°$, $[\alpha]_{5790}^{20°} - 44·0°$; $\alpha_{5461}^{20°} - 1·58°$, $[\alpha]_{5461}^{20°} - 51·2°$.

Action of Anisylmagnesium Bromide on Pyruvic Acid.—The Grignard reagent prepared from 66·5 g. of *p*-bromoanisole (2¾ mols.) was added gradually to a cooled ethereal solution of 11·5 g. of freshly distilled pyruvic acid (1 mol.). After 1 hour's boiling, and decomposition of the additive complex with ice and dilute sulphuric acid, the product from the ethereal layer was distilled in steam to remove dianisyl. By extraction of the residue with ether, 9·6 g. of crude acid were obtained, a further amount (7·5 g.) being got by extracting with ether the acid layer from which the ethereal layer had been removed after the disruption of the additive complex. The united solid was crystallised twice from benzene–acetone. Yield, 10·3 g.

r-Anisylmethylglycollic acid separated in silky needles, m. p. 128—129° (Found : C, 61·1; H, 6·0. Calc. for $C_{10}H_{12}O_4$: C, 61·2; H, 6·2%). Bougault (*Bull. Soc. chim.*, 1901, **25**, 854;

Ann. Chim., 1902, **25**, 522, 544) gives m. p. 129—130°. A trace with concentrated sulphuric acid gave a cherry-red coloration somewhat darker than that exhibited by r-phenyl-*p*-tolyl-glycollic acid under similar conditions.

The acid was also prepared by the action of the Grignard reagent from 40 g. of methyl iodide (3 mols.) on an ethereal solution of 17 g. of anisoylformic acid (1 mol.) obtained by oxidising *p*-methoxyacetophenone with alkaline permanganate (McKenzie and P. D. Ritchie, *loc. cit.*). Yield, 13 g.

Both of these methods are more practical than that by the oxidation of 4-methoxyhydratropic acid (Bougault, *loc. cit.*).

When its solution in glacial acetic acid was acted on with hydriodic acid and phosphorus, the product was a compound, m. p. 210—213°, which seemed to be identical with the compound, $C_{20}H_{20}O_4$ (m. p. 215°), described by Bougault (*Compt. rend.*, 1908, **146**, 767, 844) as being formed by the action of mineral acid on 4-methoxyatropic acid.

Resolution of r-Anisylmethylglycollic Acid.—42·8 G. of morphine (1 mol.) were dissolved gradually in a solution of 24·9 g. of *r*-anisylmethylglycollic acid (1 mol.) in 1 l. of boiling water. The crystals (A, 33 g.) which had separated over-night in the ice-chest were collected and recrystallised seven times from boiling water, rosettes of prisms of the homogeneous morphine salt (14·9 g.) of the (—)acid being obtained. The acid (5·3 g.) got by decomposing this salt with dilute sulphuric acid and extraction with ether had m. p. 146—147° and gave in ethyl alcohol : $l = 1$, $c = 3\cdot997$, $\alpha_{5461}^{19\cdot5°} - 2\cdot47°$, $[\alpha]_{5461}^{19\cdot5°} - 61\cdot8°$, whereas McKenzie and P. D. Ritchie (*loc. cit.*) give m. p. 146—147° and $[\alpha]_{5461}^{25°} - 61\cdot7°$ ($c = 4\cdot0645$). The acid underwent partial dehydration when heated at 70° under diminished pressure owing to the formation of 4-methoxyatropic acid, which takes place more readily than does the formation of atropic acid from atrolactinic acid under similar conditions. In the determination of the specific rotatory power it is advisable to conduct the drying at the ordinary temperature under diminished pressure.

The filtrate, from which A had been removed, gradually deposited rectangular crystals (17 g.), which were crystallised twice from water. The resulting crystals (11 g.) were decomposed by dilute sulphuric acid and gave an acid, m. p. 145—146°; in ethyl alcohol $[\alpha]_{5461} + 60°$ ($c = 3\cdot946$). This consisted of the almost pure (+)acid, but some 4-methoxyatropic acid was also present, as was shown by the action on potassium permanganate and on bromine water.

35. *Trypanocidal Activity and Chemical Constitution. Part IV. Derivatives of Benziminazole-5-arsonic Acid.*

By J. Garwood Everett.

The outstanding trypanocidal value of 2-thiolbenziminazole-5-arsonic acid and the corresponding arseno-compound and arylarsenic disulphide and the modification of therapeutic activity due to substitution in the thiol group having already been demonstrated, the effect of the absence of sulphur from these compounds has now been studied; the results obtained with benziminazole-5-arsonic acid and its derivatives are here recorded.

The action of chloroacetic acid and chloroacetamide on benziminazole-5-arsonic acid produced 1(or 3)-*carboxymethylbenziminazole-5-arsonic acid* and 1(or 3)-*carbamylmethyl-benziminazole-5-arsonic acid* (II) respectively. The latter acid has special interest owing to its analogy to " Tryparsamide " (I), which is of value for its action in cases where the cerebro-spinal fluid is affected. It has the advantage over " Tryparsamide " that the corresponding *arseno*-compound is soluble and therefore can be used for injection. The arseno-compound is soluble in dilute hydrochloric acid and in excess of dilute sodium hydroxide solution. The latter solubility is surprising, but is also shown by the somewhat

analogous 5 : 5'-arseno-(2-carbamylmethylthiolbenziminazole) (Part II; J., 1930, 2402). This point is of interest in view of the relationship of the compounds concerned to

$AsO(OH)_2$ $AsO(OH)_2$ or $AsO(OH)_2$

NH·CH₂·CO·NH₂   N=CH, N·CH₂·CO·NH₂   N·CH₂·CO·NH₂, N=CH

(I.)   (II.)
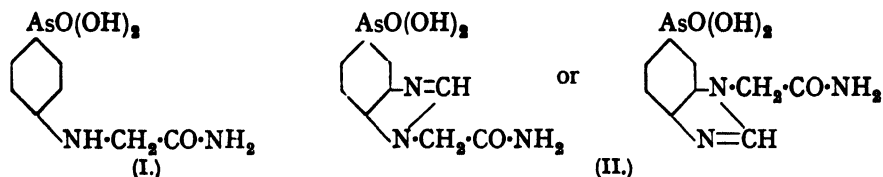
3 : 4 : 5 : 3' : 4' : 5'-hexa-aminoarsenobenzene and its *N*-methyl derivatives, which have the unexpected property of dissolving in alkali carbonate solutions, forming carbamates with the same degree of alkalinity as that of normal blood serum (Baxter and Fargher, J., 1919, **115**, 1373).

Therapeutic Results.—The above-mentioned compounds have been tested against an experimental infection of *T. equiperdum* in mice with the following results : T = maximum tolerated dose in mg./g. of mouse; c = minimum curative dose in mg./g. of mouse, and is the smallest single dose which will cause the disappearance of all trypanosomes from the peripheral blood-stream of all eight mice within seventy-two hours; r = average number of days elapsing between disappearance and reappearance of trypanosomes in the peripheral blood-stream; i = intravenous; o = oral. The relapse figures refer to the minimum curative dose (c).

		$T.$	c (8 mice).	$T/c.$	$r.$
Benziminazole-5-arsonic acid	i	1·0	0·4	2·5	7
	o	12·0	0·5	24·0	7
1(*or* 3)-Carboxymethylbenziminazole-5-arsonic acid	i	2·0	1·0	2·0	6
	o	10·0	1·0	10·0	6
1(*or* 3)-Carbamylmethylbenziminazole-5-arsonic acid	i	2·0	1·0	2·0	6
	o	10·0	1·0	10·0	6
5 : 5'-Arseno(benziminazole)	i	0·05	0·005	10·0	10
	o	5·0	0·1	50·0	6
5 : 5'-Arseno-1(*or* 3)-carboxymethylbenziminazole	i	0·1	0·025	4·0	15
	o	2·0	0·5	4·0	10
5 : 5'-Arseno-1 (*or* 3)-carbamylmethylbenziminazole	i	0·05	0·01	5·0	10
	o	>5·0	0·1	>5·0	12
For comparison.					
2-Thiolbenziminazole-5-arsonic acid	i	0·5	0·5	1·0	>30
	o	10·0	0·1	100·0	15
5 : 5'-Arseno-(2-thiolbenziminazole)	i	0·1	0·005	20·0	>30
	o	>10·0	0·05	>200·0	12
Tryparsamide	i	2·5	0·7	3·6	—
	o	14·0	0·6	23·3	—

EXPERIMENTAL.

1(or 3)-*Carboxymethylbenziminazole-5-arsonic Acid.*—Benziminazole-5-arsonic acid (9·68 g. in water, 20 c.c.) and chloroacetic acid (3·78 g. in water, 5 c.c.) were neutralised with sodium hydroxide solution, mixed, and heated at 80° for 1 hour, alkalinity being maintained by the gradual addition of 20% sodium hydroxide solution (8 c.c. required). The mixture was treated with charcoal, filtered, and rendered faintly blue (Congo-red) with hydrochloric acid. On cooling in iced water, 1(or 3)-*carboxymethylbenziminazole-5-arsonic acid* crystallised in small white nodules (4 g.), exceedingly soluble in water. It was dried at 80°, beyond which temperature it became sticky (Found : As, 24·9; N, 9·2. $C_9H_9O_5N_2As$ requires As, 25·0; N, 9·3%).

5 : 5'-*Arseno*-1(or 3)-*carboxymethylbenziminazole.*—The mother-liquor from the above reaction was added to a solution of sodium hyposulphite (62·5 g.) and sodium hydroxide (0·6 g.) in water (1250 c.c.), and the mixture kept at 55° for 1 hour. The *arseno*-compound, precipitated as a yellow amorphous powder (3·3 g.), readily soluble in sodium bicarbonate solution and in dilute hydrochloric acid, was dried in a vacuum over sulphuric acid (Found : As, 29·4; N, 10·7. Atomic ratio As : N = 1·00 : 1·95. $C_{18}H_{14}O_4N_4As_2$ requires As, 30·0; N, 11·2%).

1(or 3)-*Carbamylmethylbenziminazole-5-arsonic Acid* (II).—Prepared in the same way as the carboxymethyl compound, solid chloroacetamide being used in place of a solution of chloro-

acetic acid, this *acid* crystallised in small white prisms (4·2 g.), very soluble in water (Found in acid dried at 80° : As, 25·2; N, 13·9. $C_9H_{10}O_4N_3As$ requires As, 25·1; N, 14·0%).

5 : 5'-*Arseno*-1(or 3)-*carbamylmethylbenziminazole.*—The mother-liquor from the above reaction, treated with sodium hyposulphite and hydroxide (see above), gave the *arseno*-compound as a yellow amorphous powder (3 g.), insoluble in sodium bicarbonate solution (Found : As, 29·2; N, 16·2. Atomic ratio As : N = 1·00 : 2·97. $C_{18}H_{16}O_2N_6As_2$ requires As, 30·1; N, 16·9%).

My thanks are due to the Directors of Messrs. May & Baker, Limited, for permission to publish these results.

36. *Studies in the Phenylsuccinic Acid Series. Part XI. Interaction of the Optically Active and Inactive Diphenylsuccinic Anhydrides with Butyl Alcohol and Aniline.*

By HENRY WREN and G. LESLIE MILLER.

THE action of water and ethyl alcohol on the optically active diphenylsuccinic anhydrides has already been examined (Wren and Still, J., 1915, **107**, 1451; Wren and Williams, J., 1918, **113**, 832; Wren and Wright, J., 1929, 139).

For the further investigation of the problem *n*-butyl alcohol was selected, since it is more readily kept anhydrous than ethyl alcohol. The alcohol reacts somewhat sluggishly with *r*-diphenylsuccinic anhydride in various media, giving analytically homogeneous butyl hydrogen diphenylsuccinates in which the proportion of *r*- and *meso*-compound has been determined by comparison of their m. p.'s with those of synthetic mixtures of the substances. The amount of *meso*-derivative in the product varies from 0% to 16·5% and is greatly affected by the nature of the solvent and by the material of the vessel, the extent of isomerisation being greater in glass than in silica. With the *d*-anhydride, the percentage of inactive material has been determined polarimetrically and the question of its existence as *r*- or *meso*-form has not been examined. The influence of the two factors is very pronounced, racemisation in non-basic solvents appearing to be due almost entirely to the glass. The very marked effect in hot benzene is almost entirely due to racemisation of the *d*-anhydride before it enters into reaction, since control experiments performed in the absence of butyl alcohol show that it is optically unstable under these conditions, which have little effect on the optical activity of butyl hydrogen *d*-diphenylsuccinate. An adequate explanation of the effect appears difficult, since it is doubtful if solubility of the alkali of the glass in benzene can be assumed or if an alkali could exist as such in the presence of an acid anhydride. In the interaction of the *d*-anhydride with aniline in various solvents the influence of the material of the vessel is largely eliminated, since the reaction occurs so rapidly and under such mild conditions that the anhydride is transformed into the hydrogen ester before racemisation is appreciable. If, however, the solvent is sufficiently basic, racemisation is very pronounced. The customary assumption that an *r*-compound behaves in dilute solution as a mixture of the *d*- and the *l*-form does not appear universally valid; *e.g.*, in ethyl benzoate in silica vessels the *r*-anhydride becomes isomerised to the extent of 12·6%, whereas the percentage racemisation of the *d*-anhydride is only 1·9.

EXPERIMENTAL.

Resolution of r-*Diphenylsuccinic Acid into its Optical Antipodes.*—The resolution by brucine in aqueous solution (Wren and Still, J., 1915, **107**, 444) involves the use of very large volumes of solvent. The substitution of 50% aqueous alcohol for water gives better yields of the active acids and is much more economical of time and labour. The following experiment is typical. *r*-Diphenylsuccinic acid (50 g.) and brucine (162 g.) were dissolved in a warm mixture of water (530 c.c.) and rectified spirit (530 c.c.). The solution was filtered, seeded with brucine *d*-

diphenylsuccinate, and kept at rest at room temperature for 24 hours. Prolongation of the time of contact of crystals and solution leads to separation of brucine *l*-diphenylsuccinate. The crystalline crop (110 g.), recrystallised from 50% alcohol (5 c.c. of solvent per g. of salt), gave 90 g. of salt which, when decomposed with acid and extracted with ether, yielded 20 g. of *d*-diphenylsuccinic acid having $[\alpha]_{5461} + 390°$ in acetone. One crystallisation from water (160 c.c. per g.) yielded 13 g. of homogeneous *d*-acid. In acetone ($l = 2, c = 0.7490$), $\alpha_{5461}^{21°} + 7.09°$, $[\alpha]_{5461}^{21°} + 473.3°$; $\alpha_{5780}^{20°} + 6.21°$, $[\alpha]_{5780}^{20°} + 414.7°$.

The mother-liquor from the first crop of brucine salt yielded 18 g. of *l*-acid with $[\alpha]_{5461} - 310°$ in acetone; two crystallisations from water yielded 9 g. of the homogeneous *l*-acid. In acetone ($l = 2, c = 0.6160$), $\alpha_{5461}^{20°} - 5.80°$, $[\alpha]_{5461}^{20°} - 471.5°$; $\alpha_{5780}^{20°} - 5.08°$, $[\alpha]_{5780}^{20°} - 412.2°$.

Less satisfactory results were obtained with solvents composed of alcohol and water in the volume ratios 1 : 3 and 3 : 1.

Di-n-butyl and n-Butyl Hydrogen Diphenylsuccinates.—These were obtained by esterification of the requisite diphenylsuccinic acid with *n*-butyl alcohol containing 3% of hydrogen chloride at 100°. The excess of alcohol was removed under diminished pressure and the residue was dissolved in ether and shaken with a slight excess of dilute potassium carbonate solution. The hydrogen esters were obtained by extracting the acidified aqueous solution with chloroform.

n-*Butyl* r-*diphenylsuccinate* separates from rectified spirit in rectangular platelets, m. p. 46—47°, readily soluble in acetone, ether, benzene, chloroform, and light petroleum (b. p. 60—80°) (Found : C, 75.3; H, 7.8. $C_{24}H_{30}O_4$ requires C, 75.4; H, 7.9%).

n-*Butyl hydrogen* r-*diphenylsuccinate* crystallises from light petroleum, containing 10% of benzene, in cubic crystals, m. p. 129—130°, readily soluble in hot benzene, sparingly in hot or cold light petroleum (b. p. 60—80°), and freely in alcohol, acetone, ether, or chloroform (Found : C, 73.5; H, 6.6. $C_{20}H_{22}O_4$ requires C, 73.6; H, 6.8%).

n-*Butyl* meso*diphenylsuccinate* crystallises from rectified spirit, in which it dissolves freely when hot, sparingly when cold, in well-defined needles, m. p. 100—101°, readily soluble in acetone, ether, chloroform, benzene, and light petroleum (b. p. 60—80°) (Found : C, 75.7; H, 7.8%).

n-*Butyl hydrogen* meso*diphenylsuccinate* separates from benzene in ill-defined, hair-like crystals, m. p. 159.5—160.5°, insoluble in hot or cold light petroleum (Found : C, 73.5; H, 6.8%).

n-*Butyl* d-*diphenylsuccinate*, m. p. 64—64.5°, forms rectangular platelets from rectified spirit (Found : C, 75.4; H, 7.8%). In acetone : ($l = 2, c = 1.4675$) $\alpha_D^{19.5°} + 6.678°$, $[\alpha]_D^{19.5°} + 227.5$; ($l = 2, c = 1.0350$) $\alpha_{5780}^{20°} + 5.09°$, $[\alpha]_{5780}^{20°} + 246.1°$; $\alpha_{5461}^{20°} + 5.77°$, $[\alpha]_{5461}^{20°} + 279.5°$. In chloroform ($l = 2, c = 1.5235$) : $\alpha_{5780}^{20°} + 8.15$, $[\alpha]_{5780}^{20°} + 267.6°$; $\alpha_{5461}^{20°} + 9.18°$, $[\alpha]_{5461}^{20°} + 301.2°$.

n-*Butyl hydrogen* d-*diphenylsuccinate* crystallises from light petroleum in rectangular prisms, m. p. 93.5—94° (Found : C, 73.7; H, 6.7%). In acetone : ($l = 2, c = 1.6085$) $\alpha_D^{18°} + 9.00°$, $[\alpha]_D^{18°} + 280.0°$; ($l = 2, c = 0.9800$) $\alpha_{5780}^{17°} + 6.16°$, $[\alpha]_{5780}^{17°} + 314.2°$; $\alpha_{5461}^{17°} + 6.95°$, $[\alpha]_{5461}^{17°} + 349.6°$. In benzene ($l = 2, c = 0.7030$) : $\alpha_{5780}^{17°} + 4.93°$, $[\alpha]_{5780}^{17°} + 350.8°$; $\alpha_{5461}^{17°} + 5.58°$, $[\alpha]_{5461}^{17°} + 397.0°$.

n-*Butyl* l-*diphenylsuccinate*, m. p. 64—64.5°, resembles its antipode (Found : C, 75.4; H, 7.9%). In acetone ($l = 2, c = 1.274°$) : $\alpha_D^{19.5°} - 5.79°$, $[\alpha]_D^{19.5°} - 227.3°$.

n-*Butyl hydrogen* l-*diphenylsuccinate*, m. p. 93.5—94°, is similar to its optical antipode in preparation and properties (Found : C, 73.7; H, 6.8%). In acetone ($l = 2, c = 1.4740$) : $\alpha_D^{15.4°} - 8.22°$, $[\alpha]_D^{15.4°} - 278.8°$.

Preparation of n-*Butyl Hydrogen Diphenylsuccinates by Semihydrolysis of the Normal Esters.*—As expected from the behaviour of the optically inactive ethyl diphenylsuccinates under analogous conditions (Wren and Still, J., 1917, **111**, 1019), the butyl esters undergo isomerisation in presence of alkali and the change becomes almost quantitative under suitable experimental conditions : a solution of butyl *r*-diphenylsuccinate (3 g.) in butyl alcohol (10 c.c.) containing a little sodium butoxide became cloudy after 3 hours at room temperature and had solidified throughout after 20 hours; the dried product (2.5 g.), after crystallisation from rectified spirit, yielded butyl *meso*diphenylsuccinate, m. p. 100.5°. Similar isomerisation occurs to a less extent under the influence of aqueous-alcoholic potassium hydroxide : a solution of *n*-butyl *r*-diphenylsuccinate (17 g.) in a hot mixture of rectified spirit (255 c.c.) and water (76 c.c.) was boiled, until it was neutral, with the quantity of aqueous-alcoholic potassium hydroxide required for semi-hydrolysis. After removal of alcohol, the mixture of normal esters was extracted with ether. The aqueous solution was acidified and extracted with chloroform and the extract was shaken with concentrated sodium carbonate solution until further addition did not cause further precipitation. The precipitate consisted essentially of sodium *n*-butyl *r*-diphenyl-

succinate, from which the hydrogen ester, m. p. 128°, was obtained by acidification and crystallisation from benzene–light petroleum. The filtrate from the sodium salt yielded *n*-butyl hydrogen *meso*diphenylsuccinate. A precisely similar result was obtained with *n*-butyl *meso*-diphenylsuccinate as initial material.

Freezing Points of Mixtures of the Normal and the Hydrogen Esters.—These were determined by the method of the B.P. 1932. The temperature of the external bath required careful adjustment to enable consistent values to be obtained. The mixtures generally crystallised more definitely than the homogeneous materials.

Mixtures of *n*-butyl hydrogen *r*- and *meso*-diphenylsuccinate :

% *meso*-Ester	100	85·7	75·3	67·8	61·6	56·5	52·0	48·0
F. p.	158°	147·2°	141·3°	136·7°	130·3°	125·3°	120·2°	113·7°
% *meso*-Ester	45·2	42·6	39·3	32·4	24·4	13·8	6·0	0
F. p.	109·7°	107·2°	100·5°	97·5°	100·7°	110·8°	120°	127·5°

Mixtures of *n*-butyl *r*- and *meso*-diphenylsuccinates :

% *meso*-Ester	100	85·2	74·4	66·2	59·2	52·5	48·4
F. p.	101·05°	85·7°	80·9°	77·5°	74·5°	70·4°	68·35°
% *meso*-Ester	44·9	37·0	28·0	24·4	14·4	7·0	0
F. p.	66·1°	55·6°	28·3°	27·4°	28·0°	35·0°	46·3°

Action of n-*Butyl Alcohol on* r-*Diphenylsuccinic Anhydride in Various Solvents in Glass and in Silica Vessels.*—In each case 3 g. of the anhydride were heated with 5 c.c. of *n*-butyl alcohol (20 c.c. in the case in which no solvent was used) and 20 c.c. of solvent. The analytical purity of the mixture of *n*-butyl hydrogen diphenylsuccinates was controlled by titration with standard alkali and the composition was deduced from f. p.

The product obtained by the use of ethyl benzoate in a glass vessel was separated by treatment with aqueous sodium carbonate and ether into *n*-butyl hydrogen *meso*diphenylsuccinate, m. p. 157—160°, and *n*-butyl hydrogen *r*-diphenylsuccinate, m. p. 129—130°.

	In glass vessels.				In silica vessels.		
Solvent.	Temp.	Hours of heating.	F. p. of product.	% of hydrogen *meso*-ester in product.	Temp.	Hours of heating.	F. p. of product.	% of hydrogen *meso*-ester in product.
Butyl alcohol	100°	6	117°	8	100°	9·5	127·6	0
Benzene	100	14	127	0	80—85	12	128·0	0
Carbon tetrachloride	75	25	119	6·7	80—85	9·5	127·0	0
Dimethylaniline	100	12·5	117·5	7·7	100	13	125·5	2
Acetophenone	100	13·5	118·5	7·0	100	14	123·5	3·5
Chloroform	100	13·5	118·8	7·0	70	10	121	5
Ethyl benzoate	100	21	107·5	16·5	100	8	112	12·6
Acetonitrile	—	—	—	—	80—90	18	122·3	4

Action of n-*Butyl Alcohol on* d-*Diphenylsuccinic Anhydride in Various Solvents in Glass and in Silica Vessels.*—The anhydride (0·4 g.) was heated with 1 c.c. of *n*-butyl alcohol (5 c.c. in the case in which a solvent was not employed) and 5 c.c. of solvent as shown below. The analytical purity of the product was checked by titration with standard alkali hydroxide, and $[\alpha]_{5461}$ determined in acetone.

	In glass vessels.				In silica vessels.		
Solvent.	Temp.	Hours of heating.	$[\alpha]_{5461}$ of product.	Inact. material, %, in product.	Temp.	Hours of heating.	$[\alpha]_{5461}$ of product.	Inact. material, %, in product.
n-Butyl alcohol	100°	8	+297·1°	15·0	100°	11	+339·3°	2·9
Chloroform	100	10	+345·7	1·1	70	13	+348·7	0·5
Carbon tetrachloride	100	10	+336·0	3·9	80—85	9·5	+344·8	1·4
Acetophenone	100	10	+327·9	6·2	100	11	+342·0	2·2
Ethyl benzoate	100	17	0·0	100·0	100	8·5	+342·9	1·9
Acetonitrile	—	—	—	—	80—90	10	+344·9	1·4
Dimethylaniline	—	—	—	—	100	10·5	0·0	100
Benzene	100	14	+ 57·8	84·12	80—85	10	+346·3	1·0
,,	100	13·5	+ 74·6	77·5	—	—	—	—
,,	100	10	+ 45·7	86·9	—	—	—	—
,,	80—85	10	+108·4	69·0	—	—	—	—

Homogeneous *d*-diphenylsuccinic anhydride in acetone ($l = 2$, $c = 1.0360$) has $\alpha_{5780}^{20°} + 6.25°$, $[\alpha]_{5780}^{20°} + 301.7°$; $\alpha_{5461}^{20°} + 7.098°$, $[\alpha]_{5461}^{20°} + 342.6°$.

Behaviour of d-*Diphenylsuccinic Anhydride and* n-*Butyl Hydrogen* l-*Diphenylsuccinate when heated in Benzene in Glass Flasks.*—The anhydride (0.4 g.) was heated in benzene (5 c.c.) during 13.5 hours at 100°. After removal of the solvent the residue, m. p. 115—116°, was optically inactive, consisting of the *r*-anhydride. When *n*-butyl hydrogen *l*-diphenylsuccinate (0.4 g.) was similarly treated, the optical activity ($[\alpha]_{5461}$) was only slightly reduced, from − 320.1° to − 313.2°. The *d*-anhydride (0.4 g.), when heated in benzene (5 c.c.) during 10 hours at 100° in a silica flask, remained practically unchanged in optical activity, the product having $[\alpha]_{5461}$ + 340.9° in acetone.

Treatment of *r*-diphenylsuccinic anhydride with benzonitrile at 100° during 10 hours, followed by removal of the solvent under diminished pressure, yielded an additive *product*, $C_{23}H_{17}O_2N$, which, after being crystallised from benzene–light petroleum, melted at 218—222° after shrinking at 160—170°; the re-solidified product melted at 228—230° without previous softening (Found : C, 77.9; H, 4.9; N, 3.9. $C_{23}H_{17}O_2N$ requires C, 77.8; H, 4.8; N, 3.9%).

Interaction of d-*Diphenylsuccinic Anhydride and Aniline in Various Solvents in Glass and in Silica Vessels.*—In each case 0.276 g. of the anhydride was mixed with 0.1 c.c. of aniline and 5 c.c. of solvent at room temperature. The diphenylsuccinanilic acid produced was isolated either by removal of the solvent in a vacuum or by extraction with dilute sodium carbonate solution, followed by acidification and extraction with ether. The analytical purity was controlled by titration with standard alkali. The specific rotations were determined in acetone.

	In glass.		In silica.	
Solvent.	$[\alpha]_{5461}$.	Inactive material, %.	$[\alpha]_{5461}$.	Inactive material, %.
Acetophenone	394.6°	0.08	394.8°	0.03
Chloroform	393.5	0.3	393.8	0.3
Benzene	393.2	0.4	393.4	0.4
Carbon tetrachloride ...	390.4	1.2	391.3	0.9
Ethyl benzoate	388.8	1.5	387.6	1.6
Anisole....................	386.9	2.1	386.9	2.1
Dimethylaniline	251.1	36.4	245.5	37.8
„	251.3	36.4	—	—

Behaviour of d-*Diphenylsuccinanil when heated in Benzene and in Ethyl Alcohol.*—*d*-Diphenyl-succinanil in chloroform ($l = 2$, $c = 1.1525$) has : $\alpha_{5780} + 2.77°$, $[\alpha]_{5780} + 120.2°$; $\alpha_{5461} + 3.11°$ $[\alpha]_{5461} + 134.9°$.

The specific rotation of 0.1 g. of the anil, heated at 80·85° during 6 hours in benzene (5 c.c.) in silica and in glass, diminished only to + 133.4° and + 131.8° respectively. The products, when heated in ethyl alcohol (20 c.c.) at 75° during 10 hours, suffered slight further diminution of optical activity to + 126.3° and + 125.2° respectively.

37. *The Correlation of Flame Movement and Ionisation Current during Explosions.*

By WILLIAM A. KIRKBY.

IONISATION phenomena during explosions of mixtures of carbon monoxide and oxygen in closed cylinders have been studied by Garner and Johnson (J., 1928, 280) and Garner and Roffey (J., 1929, 1123), who obtained current–time curves for the gases during the explosions and correlated them with the emission of infra-red radiation and the speed of flame. The extinction of steady infra-red radiation was found to coincide almost exactly with that of flame. Garner and Johnson therefore suggested that the so-called " afterglow " of such explosions is not " after-burning " but is due to the recombination of ions formed by the absorption of ultra-violet radiation by the hot gases behind the flame front.

In a previous communication (J., 1931, 847), it was shown that, in certain vibratory

explosions of methane and air, there was a correspondence between the frequency of striations in the luminous gases behind the flame front and that of fluctuations in current–time curves representing the electrical conductivity of the gases; and it was concluded that each luminous band, corresponding with a forward movement of the vibrating flame, represented a recombination of ions. In continuation of this work, explosions of mixtures of carbon monoxide and oxygen ($2CO + O_2$) have been studied by using (*a*) a cylindrical explosion vessel of glass, so that direct correlation of the movement of flame and the development of an ionisation current could be obtained; and (*b*) a cylinder of phosphor-bronze, of comparable dimensions, similar to Garner's explosion vessel.

The results, in general, support Garner's suggestion that the " after-glow " can be ascribed, at least in part, to recombination of ions. Such ions, however, need not have

FIG. 1.
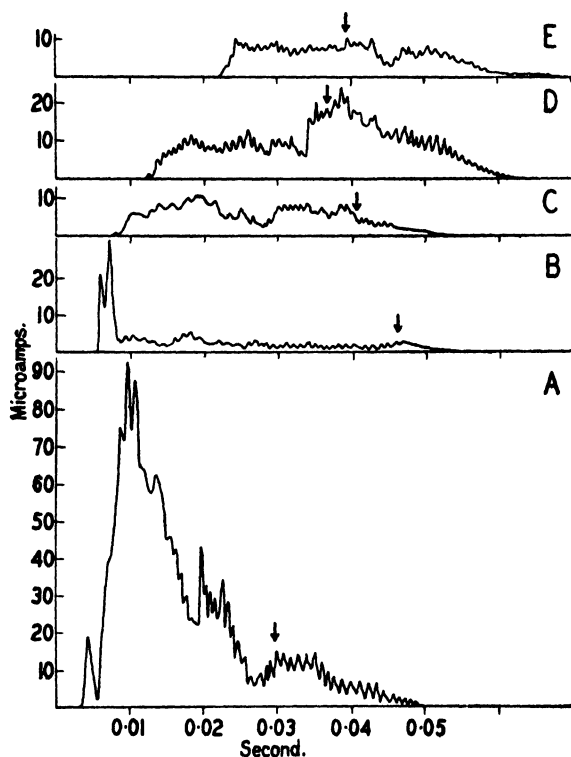
been formed exclusively, or even principally, by the absorption of ultra-violet radiation. To some extent, at least, they may have been produced as an immediate result of chemical reaction at high temperature. The visible radiation may also be accounted for, in part, by the return of electrons to their normal orbits in molecules of carbon dioxide, which have sustained excitation but not ionisation, by the chemical reactions and by the subsequent rise in temperature. For want of data, it is impossible at present to assess the relative importance of the two factors, the recombination of ions and molecular excitation, in the production of the after-glow.

Typical results are reproduced on Plates I and II, in Figs. 1 and 2, and in the tables. Records of ionisation currents were obtained (A, B, C, D, E) in turn, at each of five pairs of pointed platinum electrodes spaced at equal distances along the cylinders. Parallel sets of records were obtained, in both cylinders, with " moist " and " dried " mixtures of composition $2CO + O_2$. On each flame-photograph on Plates I and II, a diagram representing the explosion vessel has been drawn, and a broken line indicates the position of

the electrodes at which the synchronised ionisation-current curve, reproduced under each photograph, was obtained.

During the explosions in the glass cylinder (Plates I and II), an ionisation current, rising immediately to a peak value, was recorded at No. 1 pair of electrodes (see A, Plates I and II), nearest to the point of ignition which was at one end of the cylinder, as soon as the flame arrived there and considerably before the " arrest " in its movement consequent on its touching the wall of the cylinder (see Ellis and Wheeler, J., 1928, 3215). That the maximum ionisation is recorded when the flame is at this position in the cylinder, is to be attributed to the pressure prevailing then being much lower than at any subsequent stage of the explosion. The " arrest " of the flame in each explosion of the " dried " gases occurred almost exactly at the position of No. 2 pair of electrodes (see, in particular, B, Plate II). The conductivity there measured was considerably less, the temperature of the gases within the flame having been immediately reduced. During the later stages of the explosion, the conductivity just within the flame front gradually increased (Plate II, C, D, E).

At each pair of electrodes successively, after the flame-front had passed it, the conductivity recorded varied in a manner directly dependent on the variations in the rate

FIG. 2.
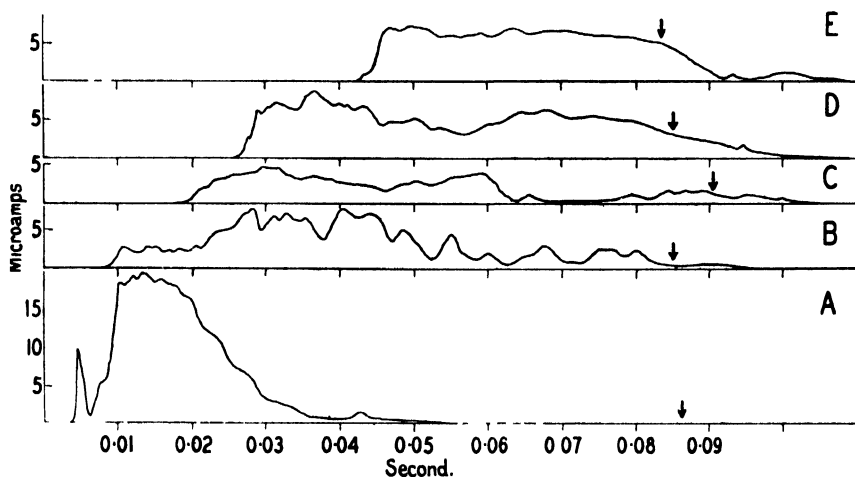
of combustion and consequent rise in temperature, as indicated by the speed of the flame at different stages of the explosion. For example, at the moment of maximum temperature, when the flame had just reached the far end of the cylinder, an increase in conductivity was recorded at each pair of electrodes.

From the synchronised records of movement of flame and development of ionisation current, it can be seen that the ionisation persists for a period which approximately corresponds, at any of the positions along the cylinder, with the duration of the " after-glow " at that position as recorded photographically. Although with the moist mixtures the degree of ionisation is greater than with the " dried," yet neither the ionisation current nor the after-glow persists as long. This is due, partly to the fact that in the moist mixtures, the flame speed being greater, the period of explosion is shorter, and consequently ionised gases are present for a shorter time; and partly to a more rapid recombination of ions in explosions of the moist mixtures, by reason of the steeper pressure gradient consequent on the more rapid movement of flame.

[Giese (*Ann. Physik*, 1882, **17**, 529) showed that, not only does the flame itself possess electrical conductivity, but the gases ascending from a stationary flame remain in a conducting state for some time after the flame has ceased to exist. The conductivity of these gases was regarded by Giese as a specific property of the products of combustion, which are in an abnormal condition, and in time assume the properties of ordinary gases. Turpin

(" Studies in the Physical and Chemical Laboratories of Owens College," Vol. I, 1893, p. 283) attempted to measure the duration of electrical conductivity in explosions of hydrogen and oxygen mixtures in a tube.]

At the same time it is to be observed that the duration of after-glow and persistence of ionisation after the flame period are less in moist than in dried mixtures. Other experiments (to be communicated later) have been carried out in a sphere, and comparative measurements made, of the intensity and amount of radiation in the visible region, which were found to be less in moist mixtures (and in those containing small amounts of hydrogen) than in dried mixtures. It has been suggested by Garner and his co-workers (J., 1929, 1123; 1931, 641) that the average duration of life of the activated carbon dioxide molecules is decreased on addition of water vapour, and the internal energy of the molecules is removed by collision, less energy being emitted as radiation. In dried gases, these activated molecules are very stable towards collisions, but can lose their energy by emission of radiation, *i.e.*, $CO_2' \longrightarrow CO_2 + h\nu$, or by resonance to other molecules of carbon dioxide, *i.e.*, $CO_2' + CO_2 \longrightarrow CO_2 + CO_2'$.

The photographs of explosions of " moist " mixtures of carbon monoxide and oxygen show that the flame vibrates with a frequency which increases as the explosion proceeds. Just prior to completion of the explosion (for the last 6 cm. of the cylinder) the frequency remains constant, and is about 1220. This is also the frequency of the fluctuations in the corresponding ionisation current–time curves and of the luminescent bands in the gases behind the flame front. These striations are found to be compression waves, as was shown previously in the case of methane–air explosions (J., 1931, 847), and each corresponds to a trough in the fluctuations of the ionisation current–time curves.

Fig 3

With " dried " mixtures the flame speed is much slower than with " moist " mixtures, there is no vibratory movement of flame, and there are no small fluctuations of constant frequency in the ionisation current–time curves as in the " moist " mixtures.

The explosions in the phosphor-bronze were slower than in the glass cylinder. The mean speeds of the flame were 920 cm./sec. for the " moist " mixtures and 390 cm./sec. for the " dried," the corresponding values in the glass cylinder being 1,750 and 640 cm./sec. In consequence, the degree of ionisation was less during the explosions in the former cylinder, though the general character of the ionisation current curves (Figs. 1 and 2) was the same for corresponding explosions.

EXPERIMENTAL.

Series I. Explosions in a Glass Cylinder.—The cylinder was 34·5 cm. long and of 2·5 cm. internal diameter, and the ends were closed by metal plates, rubber washers making gas-tight joints. An ignition plug, which could be used for ignition by either a spark or a hot wire, was fitted centrally in one end-plate, and there was a tap for evacuating the vessel in the other. The cylinder was painted dead black save for a horizontal slit throughout its length, 3 mm. wide, through which flame could be photographed. The electrodes projected 0·5 cm. within the cylinder so that there was a gap of 1·5 mm. at each pair.

A Cambridge oscillograph of the Duddell type, with a periodicity of 2000—2500, was used for recording the ionisation currents. The electrical circuit used is shown in Fig. 3. A potential of 100 volts applied to the electrodes in the cylinder, A, was supplied by the battery, B. The current through the ionised gases between the electrodes passed through the resistance, R, which was varied between 50,000 ohms and 1 megohm, according to the particular pair of electrodes in the circuit, so as to obtain the maximum deflexion on the oscillograph OSC, which was included in the anode circuit (100 volts supplied by the battery, H) of an Osram PX4
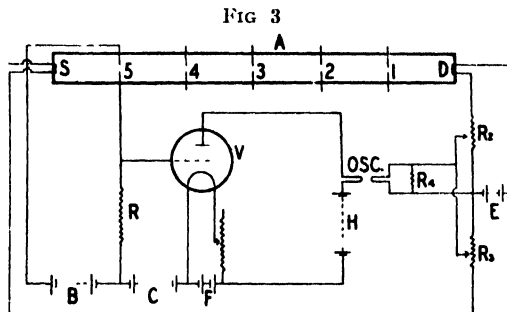
valve, V. The fall in potential due to the passage of the ionisation current through the resistance, R, was applied to the grid of the valve. C and F represent the grid-bias (17 volts) and filament (4 volts) batteries. The principle of this circuit is that described by Teegan (*Nature*, 1929, **124**, 91).

(Fig. 3 also indicates circuits used in Series II, with the phosphor-bronze cylinder, for recording the moment of ignition and the time of explosion, for which purpose a second element of the oscillograph was used. A 24-volt battery, E, supplied current for an ignition wire, D, and a screen wire, S.)

The cylinder was supported horizontally and the mixtures were ignited either by an electric spark or by an iron wire, 0·1014 mm. in diameter and 3—4 mm. long, fixed 0·5 cm. from the end of the cylinder and heated by current from a 24-volt battery. It was found that the latter method (as used by Garner and Johnson) did not always allow a direct record of the time of ignition, which is essential for correlation of the flame and oscillograph records, to be obtained by the oscillograph. Ignition might occur either before the wire fused, at the moment of fusion, or by the combustion of the ends of the wire after fusion. With spark ignition (which could be accurately recorded), and also with wire ignition in those experiments in the glass tube in which flame photographs showed that ignition and fusion of the wire occurred simultaneously, the first indication of an ionisation current was obtained at the instant that flame arrived at the electrodes used for its measurement. This fact was utilised, together with data regarding the speed of flame, to gauge the time of ignition when the hot wire was used.

Carbon monoxide was prepared by the action of sulphuric acid on formic acid, and oxygen from potassium permanganate and hydrogen peroxide. The gases were purified by passage through a series of wash-bottles containing water and dilute aqueous sodium hydroxide. The mixtures ($2CO + O_2$) were stored in glass gas-holders over water if they were to be used " moist," and in long tubes in contact with phosphoric oxide if they were to be used " dried." For filling of the explosion vessel, the " moist " mixtures were caused to bubble slowly through water in a wash-bottle; nevertheless, they could not be regarded as completely saturated with water vapour at the temperature of experiment.

Results.—(a) " *Moist* " $2CO + O_2$ *at* 18°. Measurements from the records (Plate I) are given in the following table. The values for the ionisation current in this and the other tables are not those of saturation current, and no deductions can be made from them as to the amount of ionisation. Under the particular conditions of the experiments, the ionisation currents given are those recorded when the flame is at each electrode in turn, *i.e.*, they are the values of the first maximum of each of the five current–time curves in each series of experiments. The electrodes for the measurement of ionisation currents are numbered as in Fig. 3, No. 1 being nearest to the point of ignition.

Explosions of $2CO + O_2$, " *moist* " *at* 18°.

Expt. No.	Time of explosion, sec.	Electrode No.	Ionisation current, amp. × 10⁻⁶.	Duration of ionisation current, sec.
1	0·021	1	68·0	0·035
2	0·022	2	58·4	0·036
3	0·020	3	10·6	0·021
4	0·022	4	11·2	0·025
5	0·018	5	13·6	0·033

The explosions were vibratory, the frequency of the vibrations being 1220.

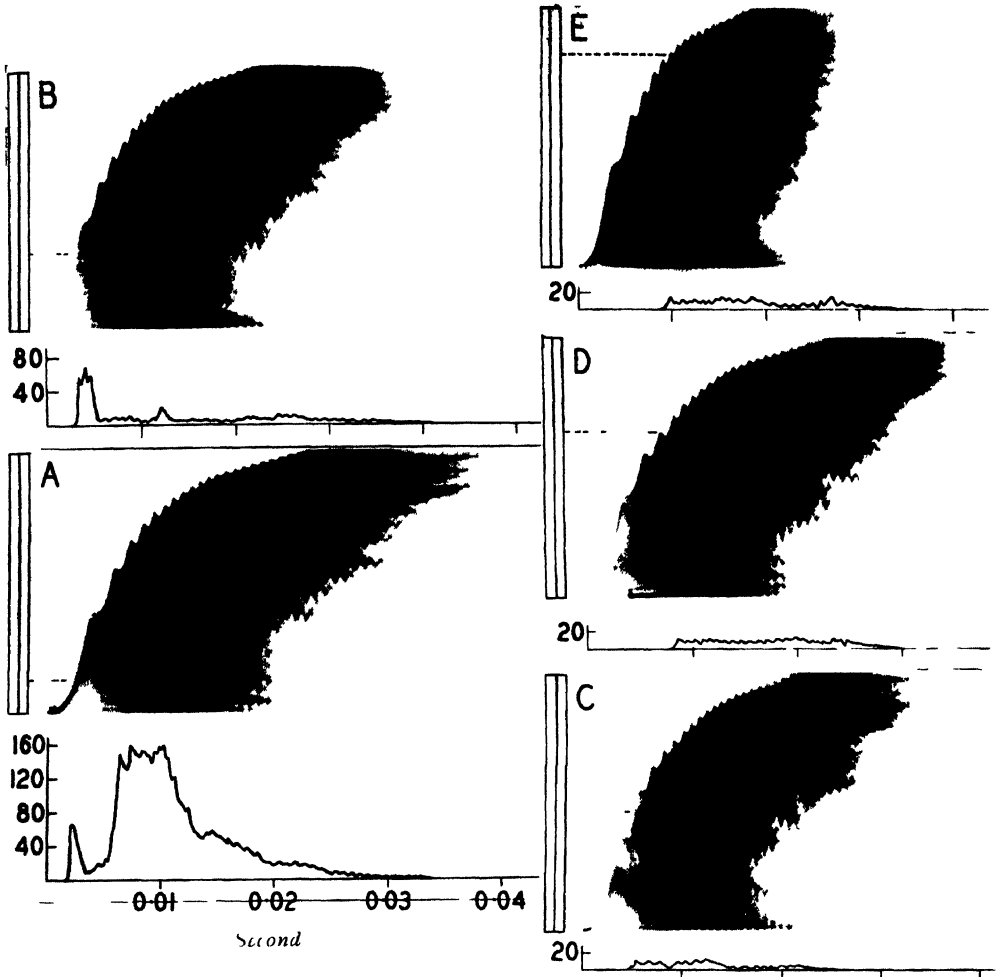(b) " *Dried* " $2CO + O_2$. Measurements from the records (Plate II) are given below :

Explosions of $2CO + O_2$ *dried over phosphoric oxide for 2 hours.*

6	0·055	1	9·3	0·038
7	0·056	2	3·5	0·055
8	0·056	3	2·4	0·065
9	0·058	4	6·9	0·085
10	0·053	5	7·7	0·065

The explosions were non-vibratory.

Series II. Explosions in a Phosphor-bronze Cylinder.—The internal dimensions of the cylinder were 35·2 cm. long and 2·5 cm. diameter. The screen-wire, S, for measuring the time of an explosion, was of tinned copper, 0·041 mm. in diameter, and carried an electric current (about 0·8 amp.) just insufficient to cause it to become visibly heated in air.

PLATE I

B

80
40

A

160
120
80
40

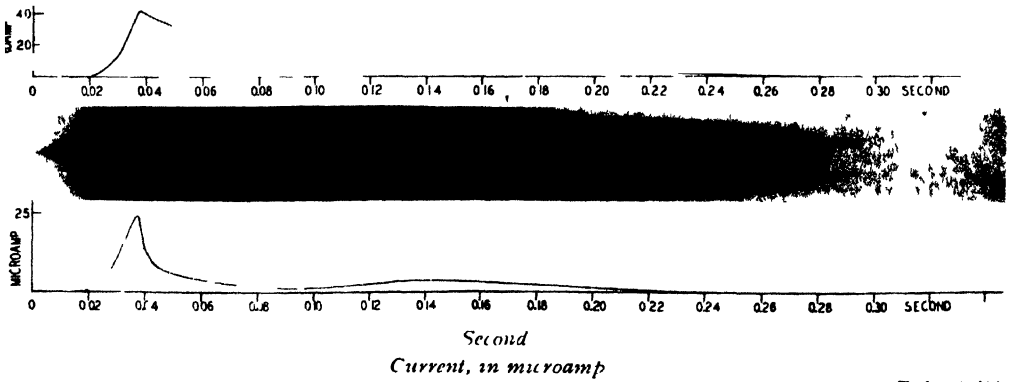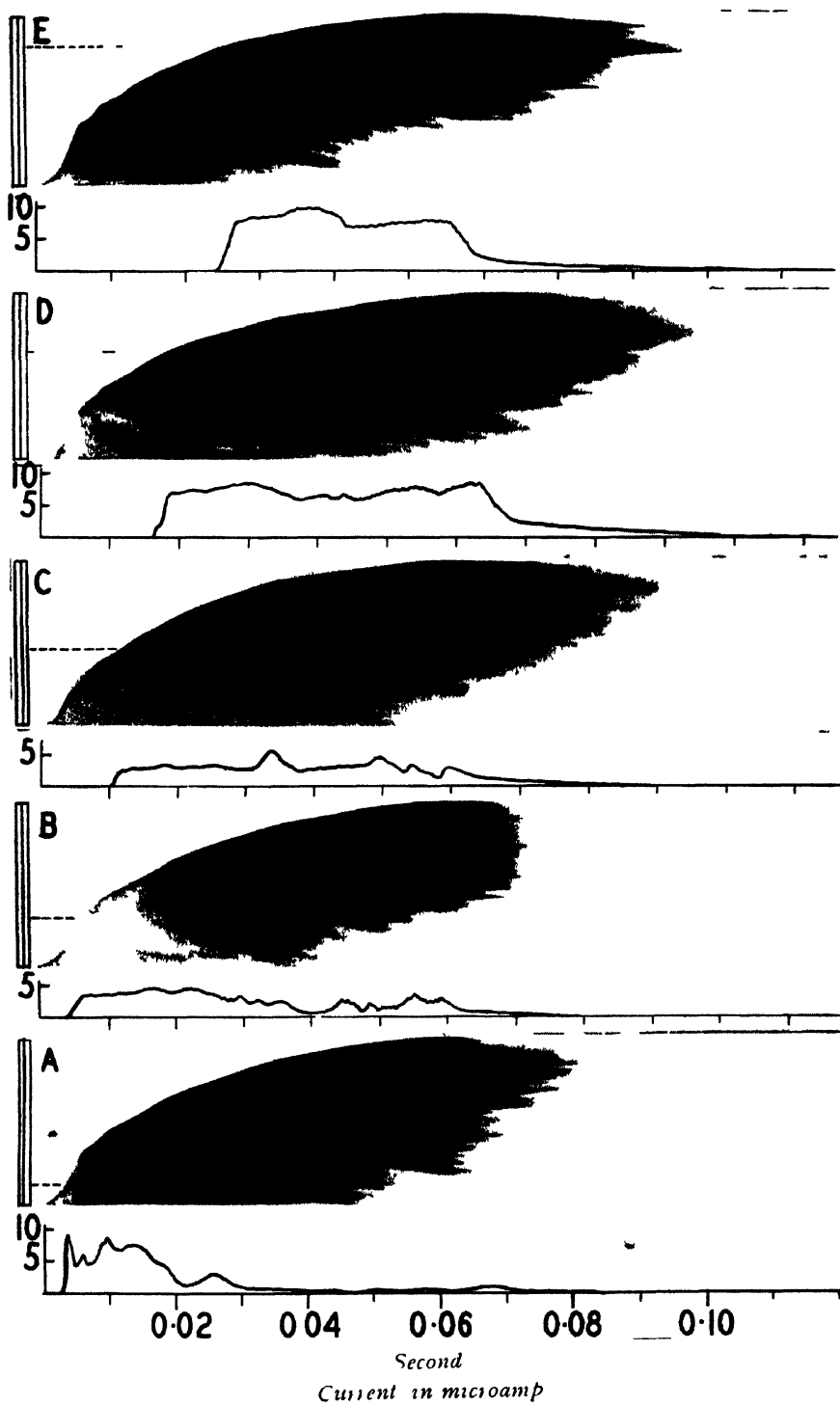0·01   0·02   0·03   0·04

Second

E

20

D

20

C

20

Current, in microamp.

40
20

0   0·02   0·04   0·06   0·08   0·10   0·12   0·14   0·16   0·18   0·20   0·22   0·24   0·26   0·28   0·30 SECOND

25

MICROAMP

0   0·02   0·04   0·06   0·08   0·10   0·12   0·14   0·16   0·18   0·20   0·22   0·24   0·26   0·28   0·30 SECOND

Second

Current, in microamp

PLATE II

Second

Current in microamp

Results.—(a) " *Moist* " $2CO + O_2$ at 17°. Measurements from the records (Fig. 1) are given in the following table. The arrow on each current–time record indicates the time of arrival of flame at the far end of the cylinder.

Explosions of $2CO + O_2$, " *moist* " *at* 17°.

11	0·030	1	19·0	0·035
12	0·046	2	21·0	0·050
13	0·041	3	6·0	0·045
14	0·037	4	5·0	0·053
15	0·039	5	10·1	0·050

The frequency of fluctuations in the ionisation currents during these explosions varied from 1000 to 1100 during the flame period, and thereafter was 900.

(b) " *Dried* " $2CO + O_2$. Measurements from the records (Fig. 2) are given below :

Explosions of $2CO + O_2$, *dried over phosphoric oxide for 2 hours.*

16	0·086	1	10·0	0·055
17	0·085	2	3·3	0·085
18	0·091	3	2·4	0·090
19	0·085	4	6·3	0·085
20	0·084	5	7·25	0·068

No regular fluctuations in the ionisation currents, indicative of vibratory explosions, were observed.

38. *The Correlation of Ionisation and Radiation in Carbon Monoxide–Oxygen Explosions.*

By WILLIAM A. KIRKBY.

THE author has already demonstrated (J., 1931, 878) an apparent connexion between the recombination of ions formed during explosion and the after-glow which may succeed the passage of flame in closed vessels. Photographic records of explosions in a sphere indicated that the after-glow was most intense slightly after the time that the ionisation was at a maximum; and that, following this maximum, the duration of the fading after-glow corresponded closely to that of the diminishing ionisation. It has now been found, however, that there is no other simple relationship. The decay of ionisation is essentially different in character from the decay of the after-glow, for it follows the law of recombination of ions, and consequently the decay of the after-glow cannot wholly be attributed to ionic recombination.

In this study, use has been made of photoelectric cells. The visible and the near infra-red radiation have been recorded separately, and measurements have been made of their variation of intensity with time.

EXPERIMENTAL.

The explosion vessel was a glass sphere, 9 cm. in diameter, as used in previous work (*loc. cit.*). Following the method originally adopted by Wilson (" Electrical Properties of Flame," p. 57, 1912) for measuring the ionisation in flames, the explosion sphere was fitted with two stout wires of platinum, diametrically opposed, which served as conductivity electrodes across a gap of 1 cm. at the centre. The mixture was ignited by a single secondary discharge from an induction coil, across a 2-mm. spark-gap formed at the centre of the sphere by two platinum wires. In each experiment the primary current of the induction coil at break was 5 amps. The passage of the flame through the sphere, as seen through a horizontal slit 3 mm. wide on its equator, was photographed on a revolving drum. The peripheral speed of the drum was obtained by photographically recording, simultaneously with the experiment, the spark of the mercury contact-breaker of an electrically-maintained tuning fork of 100 frequency.

M

The radiation from an explosion passed through a circular window, 2 cm. in diameter (the remainder of the outside of the sphere, except the equatorial window for the flame photograph, being painted black), and was then focused on the cathode of the photoelectric cell by a quartz lens.

For measurement of the visible radiation, a G.E.C. cell, KMV6, was used; this is a vacuum cell with a potassium cathode, its limits of sensitivity being at $0\cdot4$ μ and $0\cdot78$ μ, with a maximum at $0\cdot6$ μ. A Wratten No. 64 Minus Red (light) Filter, with limits of transmission at $0\cdot27$ μ and $0\cdot63$ μ, was used to cut out the near infra-red. Thus the visible radiation received by the cell extended from $0\cdot4$ μ to $0\cdot63$ μ. For measurement of the near infra-red radiation over a small range, an Oxford Instrument Company's vacuum cell, X11, was employed. This has maximum sensitivity at $0\cdot85$ μ with an upper limit at $1\cdot2$ μ. Radiation below $0\cdot74$ μ was cut out by a Wratten No. 87 infra-red filter. Thus the range of infra-red radiation measured by this cell extended from $0\cdot74$ μ to $1\cdot2$ μ and did not include the important bands at $2\cdot72$ μ and $4\cdot4$ μ (due to water and carbon dioxide molecules respectively); but, even so, these experiments showed certain differences of a minor character between the infra-red and the visible radiation.

The photoelectric current set up by the radiation was amplified and recorded on a Cambridge Duddell oscillograph by means of the circuit shown on the right-hand side of Fig. 1. The photoelectric current from the cell, P, was proportional to the intensity of the light received by it from the explosion in the sphere, A. The battery, B_2, supplied a potential of 50 volts
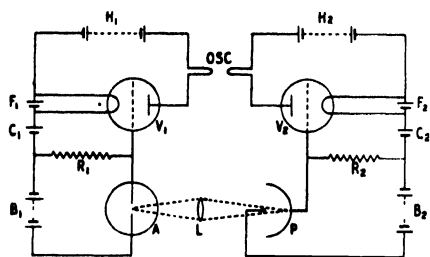
FIG. 1.　　FIG. 2.
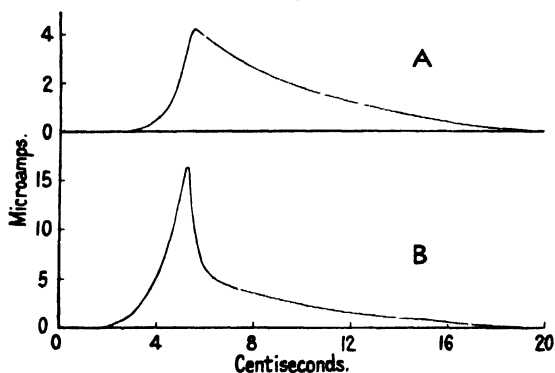
to the anode of the cell. The current passed through a high resistance, R_2, producing a change in the potential of the grid of an Osram PX4 valve, V_2, and therefore a change in the anode current which passed through the oscillograph, OSC. The value of the resistance R_2 was usually a few megohms. A potential of 100 volts was applied to the anode of the valve by the battery H_2. The valve-filament and grid-bias batteries, F_2 and C_2, were 4 volts and 17 volts respectively. The circuit was mounted within a copper box which, in turn, was inside and insulated from a second box, thus screening from electromagnetic fields the photo-cell and its connexions to the grid of the valve through the high resistance.

The method of measurement of the ionisation produced during explosions is described in detail in the preceding paper, but the circuit used to record the ionisation current for correlation with the photoelectric current is shown in Fig. 1. The ionisation current between the point electrodes in the explosion sphere, A, was amplified by a method similar to that used for the photoelectric current. The battery, B_1, supplied a potential of 100 volts to the conductivity electrodes, and the current passed through the high resistance, R_1 (a few megohms), thereby causing a potential fall proportional to the current, which was applied to the in-put of another Osram PX4 valve, V_1. The batteries, H_1 (100 volts), F_1 (4 volts), and C_1 (17 volts), were for the anode, filament, and grid bias respectively. The second vibrator of the oscillograph, OSC, was connected in the anode circuit of the valve to record the ionisation current.

As this investigation was the first of its kind, variation in experimental conditions was reduced to a minimum, and in all the experiments the gas mixture employed was $2CO + O_2$. The gases were prepared and stored as described in the preceding paper, and the degrees of dryness were also obtained as in those experiments.

Series I.

Synchronous Records of Ionisation and Visible Radiation.—Results typical of those obtained with " moist " and " dried " mixtures are shown below :

	Flame period (sec.).	Ionisation record.		Radiation record.			
Expt. No.		Time to max. current (sec.).	Max. current (10⁻⁶ amp.).	Time to max. current (sec.).	Max. current (10⁻⁶ amp.).	Energy received.* Up to max.	After max.
1 Moist	0·008	0·009	45	0·0095	5·7	8	109
2 Dried	0·038	0·039	23	0·040	7·1	24	208

* Area under the curve; given in arbitrary units.

On Plate IA is shown a typical set of three records, simultaneously taken, of the explosion of a " dried " mixture. Above and below the photograph respectively are the photoelectric and the ionisation current–time curve. The only difference of any importance in the character of these records from those of a " moist " mixture is in the length of the flame period, which is much longer when a " dried " mixture is employed. Whether the mixture be " moist " or " dried," however, the after-glow always appears during the flame period, and first begins to be intense during the later stages of the explosion when pressure is rapidly increasing. It is seen from Plate IA that the maximum in the photoelectric current, which indicates the emission of maximum intensity of visible radiation, occurs at the end of the flame period ; this, as the original photograph clearly shows, is also the most intense region of the after-glow as photographically recorded. From the results in the foregoing table, however, the maximum in the photoelectric current occurs very slightly after the time of maximum ionisation current ; and from the records on Plate IA it is seen to correspond with the steepest portion of the ionisation current decay curve, immediately after its maximum. The maximum amount of ionisation occurs at the moment of maximum temperature, at the end of the flame period, when the flame is just arriving at the wall of the sphere. At this moment, because it is also the moment of maximum pressure, the ions formed during the explosion sustain the quickest rate of recombination, and the maximum intensity of radiation due to this source is then exhibited.

Series II.

Synchronous Records of Ionisation and Infra-red Radiation.—The following results are typical of those obtained with " moist " and " dried " mixtures :

	Flame period (sec.).	Ionisation record.		Radiation record.			
Expt. No.		Time to max. current (sec.).	Max. current (10⁻⁶ amp.).	Time to max. current (sec.).	Max. current (10⁻⁶ amp.).	Energy received. Up to max.	After max.
3 Moist	0·008	0·009	54	0·012	1·2	4·0	30
4 Dried	—	0·036	24	0·039	1·0	5·5	29

The values in the above table for " maximum current " and " energy received," from the radiation record, are not comparable with similar values in the table of Series I, since the sensitivities of the two photoelectric cells were different.

The maximum in the photoelectric current from the infra-red radiation (Fig. 3, curve C) is blunt, whereas that for visible radiation was sharply pointed.

It is seen from the last table that the maximum in the photoelectric current occurs later (by 0·003 sec.) than the moment of the three coincident maxima of temperature, pressure, and ionisation current. There is a considerable increase in the infra-red emission during the period of most rapid ionic recombination, and these two phenomena may be connected. Garner and Johnson (J., 1928, 296) suggested that in their experiments the residual infra-red radiation, which was emitted after the flame had passed entirely through the explosive mixture in the cylinder, and the emission of visible radiation may be complementary phenomena. The radiation emitted on recombination of ions will be absorbed by certain carbon dioxide molecules, bringing about a process analogous to that of " sensitised fluorescence " ; the absorbed radiation, undergoing degradation, will stimulate the vibrational energy of the molecules, with consequent emission in the near infra-red region.

The outstanding feature of the results, however, is neither the delayed incidence of the radiation maxima nor the difference in their shape, but the pronounced lack of similarity in the characters of both radiation curves as compared with the ionisation curve. The difference in character is fundamental, and yields proof that the after-glow in gaseous explosions is chiefly due to some cause other than the recombination of ions ; though it remains true that the period

during which this cause is operative is closely identified with the period of ionic recombination. Since the number of molecules formed during the chemical reaction which sustain excitation will be much larger than the number which simultaneously are ionised, the after-glow may be attributed to the return of the excited molecules to a normal state.

Two of the synchronous records of the explosion of a " dried " mixture are shown in Figs. 2 and 3. B and D are the ionisation curves, and the radiation curves are A (visible) and C (infra-red). They were obtained by photographically enlarging to several times their original size the oscillograph records of the amplified currents, and thence calculating and replotting,
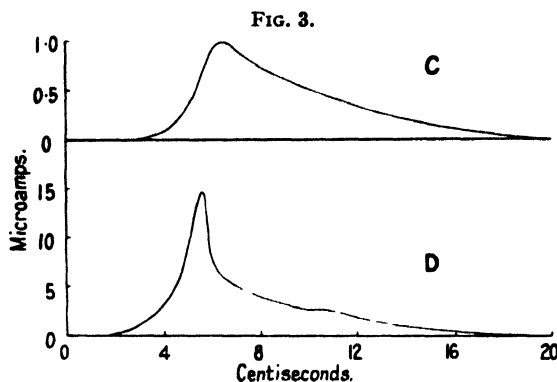
FIG. 3.

millisecond by millisecond, the actual currents entering the amplifiers. The rise of the curves from zero to their maxima calls for little comment now; the principal conclusion of this paper is founded upon the shape of the curves as they decay from their maxima, or just after, to zero.

The decay portions of some of these curves for a period of 30 millisecs. after maximum, the first ordinate being neglected, are expressible by (1) $C_{vr} = K_1 t^{0.021} e^{-0.022t}$, for visible radiation, where C is current in microamps., and t is time in millisecs. after maximum current, (2) $C_{ir} = K_2 e^{-0.0202t}$ for the infra-red radiation, (3) $C_i = K_3 t^{-a}$, where the value of a is 0.38—0.40, for the ionisation current. The exponential factor in the first expression is dominant, and the decay of radiation in the two regions of the spectrum is essentially of the same character.

If the visible radiation were due to the recombination of ions, the intensity of the radiation would vary with the rate of recombination, and be proportional to the rate of change of current, which is given by $dC_i/dt = -aK_4 t^{-(a+1)}$. The expression for the decay of ionisation is of quite a different character from that for the decay of visible radiation.

Equations in ascending powers of t, obtained by a method based on the theory of differences, show that there can be no simple correlation of visible radiation with ionic recombination; e.g., the decay of visible radiation may be written, $C_{vr} = 4.22 - 0.09t + 0.001t^2$, whereas $C_i = 17.36 - 3.13t + 0.40t^2 - 0.03t^3 + 0.001t^4$, and the rate of change of current during the decay period of ionisation is given by $-dC_i/dt = 3.13 - 0.8t + 0.09t^2 - 0.004t^3 + \ldots$.

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39. *Physicochemical Studies of Complex Formation Involving Weak Acids. Part XIII. The Reactions of Malonic Acid with Typical Metallic Bases.*

By H. T. S. BRITTON and MAURICE E. D. JARRETT.

ACCORDING to Britton (J., 1925, **127**, 1909), K_2 of malonic acid at 18° is 4.4×10^{-6}, from which it might be expected that normal combination is not possible with those metallic bases which are precipitated at p_H values below $p_{K_2} + 2$, *i.e.*, p_H 7.36. Yet it is possible to prepare well-defined crystalline malonates from, *e.g.*, zinc and copper hydroxides, which undergo precipitation from sulphuric, hydrochloric, or nitric acid solution on reaching p_H 6.8 and 5.3 respectively. Combination with such bases, therefore, must be accompanied by some kind of complex formation which produces a substantial diminution in the metallic-ion concentration in order to prevent the separation of some of the base on dissolution of the salt in water.

As the methods used by Riley and his co-workers (J., 1928, 2985; 1929, 1307, 2006; 1930, 1307, 1642; 1931, 1998) in investigating the malonates and substituted malonates of zinc and copper, and by Sidgwick and Lewis (J., 1926, 2538) with beryllium malonate, do not furnish any precise information regarding the ions actually taking part in the equilibria, especially hydromalonate ions, we have studied particularly the concentrations of hydrogen ions in order to elucidate the equilibria from which they arise.

<div align="center">EXPERIMENTAL.</div>

Neutralisation of Malonic Acid with Metallic Bases.—Solutions were prepared that were either 0·04M (Table IA) or 0·02M (Table IB) with respect to malonic acid, free and combined, and contained increasing amounts of the bases indicated. The specific conductivities were measured at 25°, and the p_H values at 18° by an electrometric method, the glass electrode in conjunction with an electrometer triode valve being used in those instances where the hydrogen
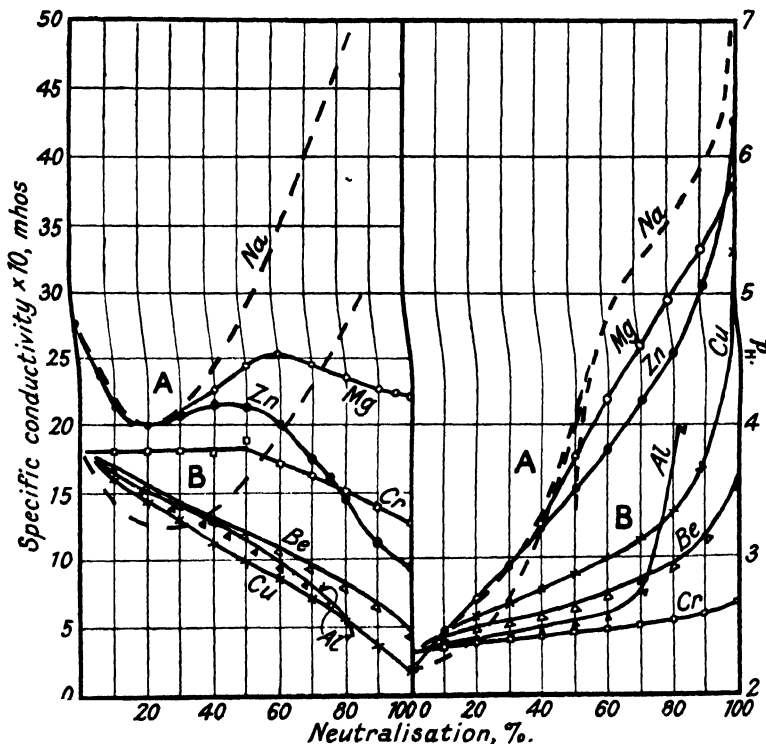
<div align="center">*Neutralisation, %.*</div>

and the quinhydrone electrodes were inapplicable. The data recorded in Table I for each successive 10% of neutralisation (N, %) by the various bases are compared with those set up by similar molecular proportions of sodium hydroxide. In the fig. (left) the specific conductivities are compared with those corresponding to the neutralisation with sodium hydroxide (broken line), whilst in the right-hand diagram the p_H values are similarly plotted.

Some difficulty was experienced in dissolving the weaker bases at room temperature by prolonged mechanical agitation. Recourse to heating was avoided, where possible, as it was considered that such treatment would lead to a loss in the reactivity of the base towards malonic acid, particularly with its second stage.

The magnesium and zinc solutions were prepared by adding the requisite amounts of the oxide to malonic acid solutions and heating on a water-bath; but as only 95% and 90% respectively of the acid could thus be neutralised, solutions corresponding to 100% neutralisation were prepared from the isolated normal salts, $ZnC_6H_4O_8,2H_2O$ and $MgC_6H_4O_8,2H_2O$.

For the preparation of the aluminium and chromium solutions an acidic aluminium malonate (Al, 9·1; $C_3H_2O_4''$, 63·11%) and the heptahydrate of normal chromium malonate (Cr, 19·59; $C_3H_2O_4''$, 57·2%) were isolated by saturating 10% malonic acid solutions with the freshly

TABLE I.

A. *Neutralisation of 0·04M-Malonic Acid.*

N, %.	NaOH. p_H.	$10^3\kappa$.	Mg(OH)₂. p_H.	$10^3\kappa$.	Zn(OH)₂. p_H.	$10^3\kappa$.	N, %.	NaOH. p_H.	$10^3\kappa$.	Mg(OH)₂. p_H.	$10^3\kappa$.	Zn(OH)₂. p_H.	$10^3\kappa$.
0	2·17	2·79	2·17	2·79	2·17	2·79	60	4·80	3·32	4·17	2·53	3·79	2·00
10	2·24	2·21	2·45	2·12	2·45	2·15	70	5·19	3·96	4·61	2·44	4·17	1·74
20	2·47	2·01	2·69	1·99	2·72	2·00	80	5·53	4·64	4·95	2·33	4·55	1·43
30	2·72	2·12	2·96	2·07	2·96	2·07	90	5·90	5·30	5·32	2·26	5·07	1·13
40	3·21	2·41	3·26	2·27	3·19	2·16	100	9·06	5·94	5·85	2·20	6·27	0·94
50	4·00	2·80	3·75	2·44	3·52	2·13							

B. *Neutralisation of 0·02M-Malonic Acid.*

N, %.	NaOH. p_H.	$10^3\kappa$.	Cr(OH)₃. p_H.	$10^3\kappa$. obs.	calc.	Be(OH)₂. p_H.	$10^3\kappa$. obs.	calc.	Al(OH)₃. p_H.	$10^3\kappa$. obs.	calc.	Cu(OH)₂. p_H.	$10^3\kappa$. obs.	calc.
0	2·35	1·82	2·35	1·82	1·82	2·35	1·82	1·82	2·35	1·82	1·82	2·35	1·82	1·82
10	2·45	1·41	2·40	1·80	1·63	2·42	1·70	1·56	2·37	1·65	1·66	2·46	1·59	1·40
20	2·67	1·27	2·41	1·83	1·60	2·49	1·54	1·33	2·42	1·51	1·52	2·58	1·39	1·07
30	2·94	1·30	2·41	1·78	1·58	2·53	1·41	1·20	2·47	1·37	1·38	2·68	1·24	0·85
40	3·36	1·39	2·43	1·78	1·53	2·59	1·28	1·05	2·53	1·25	1·20	2·77	1·11	0·69
50	4·10	1·59	2·47	1·78	1·37	2·66	1·15	0·89	2·55	1·12	1·15	2·88	0·98	0·53
60	4·81	1·94	2·48	1·70	1·34	2·74	1·02	0·75	2·60	0·98	1·02	3·00	0·85	0·41
70	5·12	2·32	2·51	1·59	1·27	2·88	0·87	0·53	2·77	0·80	0·69	3·14	0·71	0·29
80	5·42	2·69	2·55	1·51	1·16	2·96	0·72	0·41	3·71	0·49	0·10	3·35	0·55	0·18
90	5·91	3·07	2·59	1·38	1·04	3·16	0·56	0·28	—	—	—	3·70	0·36	0·08
100	—	—	2·68	1·27	0·84	3·57	0·375	0·11	—	—	—	5·31	0·16	0·01

precipitated hydroxides, heating for some hours in a water-bath, filtering the solution, evaporating it to dryness, and drying at 100° for some hours. The residue was extracted with ether and redried at 100° for 6 hrs. During preparation, both substances passed through a syrupy condition, the first being finally obtained as a very hard white amorphous substance, and the second as an amorphous, dark green, friable mass (cf. Werner, J., 1904, **85**, 1438).

The hydroxides were precipitated with ammonium hydroxide from hot chloride solutions, washed with dilute ammonia until free from chloride, and then with water until free from ammonia. Sidgwick and Lewis (*loc. cit.*) obtained turbid solutions of beryllium malonate by dissolving basic beryllium carbonate in solutions of malonic acid, but clear solutions can be obtained by dissolving the so-called crystalline beryllium hydroxide (produced by boiling dilute alkaline beryllate solutions, see Britton, *Analyst*, 1921, **46**, 359) in malonic acid solution with gentle heating on a water-bath. 0·02M-Malonic acid dissolved more than the equivalent quantity of beryllium hydroxide, and data obtained with such clear basic solutions are given below :

N, %.	Composition of solute.	p_H.	$10^3\kappa_{25°}$.	(a).	(b).
100	BeO,C₃H₄O₄	3·57	0·375	9·38	9·38
110	BeO,0·91C₃H₄O₄	4·69	0·267	6·68	6·07
120	BeO,0·83C₃H₄O₄	5·05	0·288	7·20	6·00
130	BeO,0·77C₃H₄O₄	5·29	0·321	8·03	6·19
140	BeO,0·71C₃H₄O₄	5·59	0·409	10·23	7·12

The last two columns give the equivalent conductivities calculated with respect to the concentrations of (a) malonate and (b) beryllium. For a solution of beryllium malonate of concentration comparable to that corresponding to the first line of the table, Sidgwick and Lewis found Λ = 7·51, and it would appear from the table that their beryllium malonate must have been slightly basic; this also seems probable in view of their method of preparing the solutions (from the basic carbonate).

The copper solutions were prepared in the cold by dissolving copper malonate in the acid. The trihydrated salt was obtained by dissolving pure copper hydroxide, prepared by Dawson's method (J., 1909, **95**, 370), in a 20% excess of 10% solution of malonic acid on a water-bath; after partial evaporation, small, well-defined crystals separated on standing. They were purified by recrystallisation from 0·2—0·4% malonic acid solution, washed, dried, powdered, and re-washed with water and alcohol (Found : Cu, 29·04; C₃H₂O₄″, 44·5. Calc. : Cu, 28·96; C₃H₂O₄″, 44·4%). The copper was determined gravimetrically as oxide, and the malonate volumetrically by direct titration of a boiling solution to phenolphthalein. Attempts to determine the copper iodometrically led to low and variable results owing to complex formation :

by adding an excess of sodium malonate to copper sulphate the concentration of copper ions can be so depressed that excess of potassium iodide fails to produce a precipitate.

It was intended to study the reaction between an extremely weak base, *viz.*, ferric hydroxide, and malonic acid, but much difficulty was experienced in preparing a complete series of solutions owing to the limited solubility of the base and the ease with which the salt undergoes hydrolysis on heating. Two solutions, both giving p_H *ca.* 2·4, were obtained : (*a*) 0·024M-malonic acid containing half the amount of hydroxide required for the normal salt, and (*b*) 0·0432M-malonic acid containing two-thirds of the amount. The latter was prepared directly from a pale green powder of composition $Fe_2(C_3H_2O_4)_3,2Fe(C_3H_3O_4)_3,1·5H_2O$ (Found: Fe, 19·16; $C_3H_2O_4''$, 78·0%), obtained by saturating malonic acid solution at 100° with pure, freshly precipitated ferric hydroxide, evaporating the solution to dryness at room temperature, drying in air, grinding the solid, and extracting it with boiling ether; such a substance can scarcely be regarded as a definite acid salt. Dissolution in water was slow at the ordinary temperature, giving a green solution, and warming caused hydrolysis with separation of a brown precipitate, which, however, redissolved on cooling and shaking. Its ionisation was abnormal, for potassium thiocyanate yielded only a very pale coloration : none of the iron was in the reduced state. Solution (*a*), which was prepared from the same substance and malonic acid, had $\kappa = 1·734 \times 10^{-3}$ mho, indicating that the greater part of the acid was free.

The calculated specific conductivities given in Table IB were deduced from the p_H values, it being assumed that only the first-stage dissociation of malonic acid was involved, and that the contribution due to the ionised acid, $H_2M = H^{\cdot} + HM'$, is given by $\kappa_{calc.} = [H^{\cdot}](l_{H^{\cdot}} + l_{HM'})/1000$ ($l_{H^{\cdot}} = 349·7$, $l_{HM'} = 58·9$; see Vogel, J., 1929, 1486). Such an assumption is justified by the position of the p_H curves (see fig.) of the weak bases, *viz.*, chromium, beryllium, aluminium, and copper, with respect to the second section of the sodium curve, which gives the p_H values that would obtain with weak bases if (*a*) they reacted normally with malonic acid and (*b*) their salts were completely ionised. The observed and the calculated specific conductivities during the reactions with the weak bases (Table IB) are of the same order, the calculated being, in general, but slightly smaller than the actual conductivities. It appears that the hydrolysed malonic acid is responsible for the major portion of the conductivity of the solutions, and therefore that the products of the combination of the weak bases and the malonic acid are but feebly ionised.

The conductivity curves (*A*) corresponding to the two stronger bases, magnesium and zinc hydroxides, show, as do also the p_H curves, that the reaction of malonic acid with the first 0·5 equiv. of base tends to be normal, in that the curves almost coincide with the sodium curve, the variations in specific conductivity introduced by the different mobilities of the kations being negligible at such dilutions. This shows that the bases are able to combine with the first stage to form magnesium and zinc hydrogen malonates, which ionise to an extent similar to sodium hydrogen malonate at the same dilution. Between 25 and 50—60% neutralisation, the conductivities fall below that of the sodium salt and, after attaining maxima, decrease as more magnesium and zinc malonate are formed. The fact that zinc hydroxide is a weaker base than magnesium hydroxide is apparent from the greater diminution in conductivity in the case of zinc. Except for the p_H values of magnesium and zinc malonate solutions, *i.e.*, at 100%, the weakness of magnesium and zinc hydroxides compared with that of sodium seems also to be reflected in the relative positions of the p_H curves between 50 and 100% neutralisation, the zinc curve again lying below that of magnesium. As the p_H values result from the equilibrium $HM^{\cdot} \rightleftharpoons H^{\cdot} + M''$, it follows that the lower p_H values represented by the zinc and magnesium curves indicate much lower ratios of malonate to hydrogen malonate ions. This must be attributed chiefly to diminished concentrations of malonate ions which originate from the substances formed by the reaction of the zinc and magnesium hydrogen malonates with further amounts of the respective base. The effect of the much weaker second stage is thus made apparent.

The conductivity and p_H curves (*B*) of the series of the yet weaker bases, when compared with the appropriate sodium curves, show that the equilibrium $H_2M \rightleftharpoons HM' + H^{\cdot}$ is now the controlling factor.

In view of the increasing tendency exhibited by the stronger bases, *viz.*, magnesium and zinc hydroxides, to combine normally with the first equivalent of malonic acid, the conductivities and p_H values of solutions of magnesium, zinc, and copper hydrogen malonates were determined in a series of dilutions. Col. 1 of Table II gives v, the number of litres containing 1 g.-equiv. of the metallic base. The p_H values (col. 2) were measured at 18° and the conductivities at 25°. The columns headed " $\alpha,Mg(HM)_2$," etc., give the apparent degrees of ionisation, *viz.*, the conductance ratio, Λ_v/Λ_∞ ; Λ_∞ for magnesium, zinc, and copper hydrogen malonates was taken

as 111·9, 114·9, and 113·8, respectively, these values being based on the mobility of the hydro-malonate ion, 58·9 (Vogel, J., 1929, 1476), and on those of the respective metallic ions (Landolt-Börnstein, " Tabellen "). The degrees of ionisation of magnesium hydrogen malonate are compared with those of its sulphate and chloride under similar conditions, and those of the zinc and copper hydrogen malonates are each similarly compared with two salts of the metal.

The p_H values of the magnesium and zinc solutions are slightly lower than those of sodium hydrogen malonate solutions at the same concentrations. From the dissociation constants,

TABLE II.

Magnesium hydrogen malonate.

v.	p_H.	$\kappa \times 10^4$.	Λ,Mg(HM)$_2$.	a,Mg(HM)$_2$.	Λ,MgM.	a,MgM.	a,MgSO$_4$.	a,MgCl$_2$.
25	3·78	25·52	63·8	0·57	34·2	0·31	0·60	0·87
50	3·89	14·15	70·8	0·63	42·4	0·38	0·68	0·90
100	4·00	7·73	77·3	0·69	52·3	0·47	0·75	0·95
200	4·10	4·26	85·7	0·76	63·6	0·57	0·82	0·97
400	4·24	2·30	92·0	0·82	77·4	0·69	0·87	0·97
800	4·58	1·25	100·0	0·90	88·4	0·79	—	—

Zinc hydrogen malonate.

v.	p_H.	$\kappa \times 10^4$.	Λ,Zn(HM)$_2$.	a,Zn(HM)$_2$.	Λ,ZnM.	a,ZnM.	a,ZnSO$_4$.	a,Zn(NO$_3$)$_2$.
25	3·48	21·74	54·3	0·47	14·7	0·13	0·54	0·83
50	3·63	12·39	61·8	0·54	18·5	0·16	0·62	0·87
100	3·73	7·16	71·3	0·62	23·9	0·21	0·70	0·88
200	3·89	4·05	81·0	0·71	31·5	0·27	0·77	0·90
400	4·06	2·34	92·4	0·80	42·7	0·37	0·82	0·91
800	4·24	1·25	100·0	0·87	55·7	0·49	—	—

Copper hydrogen malonate.

v.	p_H.	$p_{Cu^{..}}$.	$\kappa \times 10^4$.	Λ,Cu(HM)$_2$.	a',Cu(HM)$_2$.	a,Cu(HM)$_2$.	a,CuSO$_4$.	a,CuCl$_2$.
50	2·84	2·75	10·04	50·2	0·18	0·44	0·62	0·87
100	3·00	2·93	6·56	65·6	0·24	0·58	0·73	0·90
200	3·17	3·13	4·14	82·8	0·30	0·73	0·81	0·93
400	3·34	3·31	2·56	102·4	0·39	0·90	0·85	0·95
800	3·57	3·44	1·50	120·0	0·58	1·05	—	—

Copper malonate.

v.	p_H.	$p_{Cu^{..}}$.	Λ,CuM.	a',CuM.	a,CuM.	$p_{[Cu^{..}IOH^{.}]^2}$.
25	5·54	3·07	—	0·009	—	20·2
50	5·50	3·38	4·05	0·010	0·036	20·6
100	5·48	3·59	4·25	0·010	0·037	20·9
200	5·36	3·79	4·76	0·013	0·042	21·3
400	5·26	3·96	5·75	0·017	0·051	21·7
800	5·19	4·24	7·34	0·019	0·064	22·1

$K_1 = 10^{-2·70}$ and $K_2 = 10^{-5·86}$, obtained by Britton, it would appear that the p_H of a sodium hydrogen malonate solution should be approximately 4·03 but his constants refer to 0·023M-malonic acid. A quinhydrone titration of 100 c.c. of $M/1600$-malonic acid with 0·00495N-sodium hydroxide at 18° gave slightly smaller constants, viz., $K_1 = 10^{-3·03}$ and $K_2 = 10^{-5·75}$, and the p_H at the mid-point, i.e., corresponding to a solution of 0·000555M-sodium hydrogen malonate, was 4·68. Such a concentration is a little lower than those of magnesium, zinc, and copper hydrogen malonates at $v = 800$. It may be noted that the equation $K_1K_2[H^+]^2$, as assumed by Auerbach and Smolczyk (Z. physikal. Chem., 1924, **110**, 83), does not hold at such low concentrations, for it is here that the hydrogen-ion concentration is not negligible when compared with either K_1 or the concentration of the salt (see Britton, J., 1925, **127**, 1909). Calculation of K_2 from the p_H values and $K_1 = 10^{-3·03}$ by means of the general formula (Britton, loc. cit.) gives $K_2 = 10^{-5·86}$, which agrees fairly well with the values of K_2 obtained from the p_H values prevailing during the progressive conversion of sodium hydrogen malonate into the normal malonate.

The fact that both magnesium and zinc hydrogen malonates ionise largely as normal salts is evident from a comparison of their degrees of ionisation with those of salts formed from strong acids, which were computed from the conductivities given in the International Critical Tables. Thus it is seen that a,Mg(HM)$_2$ is but slightly lower than a,MgSO$_4$, whilst a,MgSO$_4$ is appreciably smaller than a,MgCl$_2$; the latter inequality is probably to be associated with the slight weakness

of sulphuric acid in its second stage of dissociation, K_2 being 2×10^{-2}, and it is also probable that this is the reason why the ionisation of magnesium hydrogen malonate should be comparable with that of magnesium sulphate, the stage of the malonic acid involved having a constant of 2×10^{-3}. Similar remarks apply to the comparison of the zinc salts. The equivalent conductivities of magnesium, zinc, and copper malonates and their conductance ratios, α,MgM, etc., obtained by Riley and Fisher (J., 1929, 2006) and Ives and Riley (J., 1931, 1998), are inserted to show that the ionisation of these salts is considerably less than that of the respective hydrogen malonates and, moreover, that, when compared with one another, α,MgM $>$ α,ZnM $>$ α,CuM, which brings out clearly the effect of the strengths of the three metallic bases.

It might be held that consideration should have been given to the possible effect of the subsequent ionisation of the hydromalonate ion and also of any free malonic acid due to hydrolysis. Calculations, based on the p_H values and the mobilities of the hydrogen, hydromalonate, and malonate ions, reveal, however, that these effects are relatively small for magnesium hydrogen malonate, slightly greater for the zinc salt, and, owing to the low p_H values, comparatively large for copper hydrogen malonate; *e.g.*, in the dilutions investigated, the corrected conductance ratios range from 0·56 to 0·81 for the magnesium salt, compared with 0·57—0·90 as given in Table II, whereas for the zinc salt they vary from 0·44 to 0·77 instead of 0·47 to 0·87.

The low p_H values of the copper hydrogen malonate solutions indicate that much of the malonic acid had failed to combine with the weak base, and consequently the conductance ratios, α,Cu(HM)$_2$, can have no real significance. It was found that the potentials set up when a copper electrode was immersed in these solutions were quite steady and reproducible, and col. 3 gives the negative exponent to the base 10 of the copper-ion concentrations calculated therefrom. In the column headed α',Cu(HM)$_2$, the ratios of [Cu$^{··}$] to salt concentration are much smaller than the corresponding conductance ratios, and evidently indicate the extent to which the unhydrolysed copper hydrogen malonate was ionised. The retention of copper hydroxide in these solutions is seen to be possible from a consideration of the ionic products, [Cu$^{··}$][OH$'$]^2, which are much smaller than the solubility product of copper hydroxide, *viz.*, *ca.*10^{-20}.

The copper electrode, which was in the form of a small copper plate, was covered with a fine bright deposit of copper from a 10% solution of copper sulphate using a cathodic *C.D.* of about 1 amp./dm.^{2}. When tested in 0·01M-copper sulphate, which was taken as 62·9% ionised (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 475), a normal electrode potential (N-H $= 0$) of $+$ 0·341 volt at 18° was obtained. Hydrogen was bubbled through the electrode chamber during the measurement of the *E.M.F.* of the cell, the junction liquid being a saturated solution of potassium chloride, and the normal calomel electrode being the standard half-element.

The last section of the table referring to copper malonate solutions shows that the apparent degree of ionisation, α,CuM, of the normal salt is exceedingly small, and once again α',CuM $=$ [Cu$^{··}$]/[CuM] is still smaller. These solutions, unlike those of the acid salt, were on the verge of precipitating copper hydroxide, as will be seen from the values of $p_{[\mathrm{Cu}^{··}][\mathrm{OH}']^2}$ given in the last column, although there appears to be a distinct tendency for the product of the ionic concentrations to fall below the solubility product as the dilution of the salt is increased.

DISCUSSION.

The electrometric curves in the fig. show clearly that, although the majority of the bases studied are able to combine with malonic acid as far as its first stage of ionisation is concerned to an extent depending upon the precipitation p_H of the base in question (see Britton, J., 1925, **127**, 2110, 2120, 2148; Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 531) and the magnitude of K_1, yet they do not combine with the second stage in a strictly normal way. This is even true of the strongest base investigated, *viz.*, magnesium hydroxide, which does not begin to be precipitated until p_H 10·5 is reached; as this is higher than $p_H = p_{K_1} + 2 = 7·36$, the acid should have ample scope for complete neutralisation with this base, but Table I shows that the p_H of 0·04M-magnesium malonate is only 5·85, whereas the p_H of 0·04M-sodium malonate solution is 9·05. A p_H value of 5·85 indicates that the solution contains hydromalonate ions and malonate ions in approximately the ratio 1 : 3, and therefore that the former ions originate from equilibria represented by

$$2\mathrm{MgM} + 2\mathrm{H_2O} \rightleftharpoons 2\mathrm{Mg(OH)HM} \rightleftharpoons \mathrm{Mg(HM)_2} + \mathrm{Mg(OH)_2}.$$
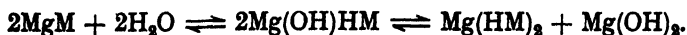
With a weaker base, such as copper hydroxide, combination with the second stage

becomes very limited and even the reaction with the first stage is incomplete. This would be expected from the p_H (*ca.* 5) at which copper hydroxide normally begins to be precipitated and K_1 and K_2 of the acid. That some malonic acid fails to combine in a copper hydrogen malonate solution, is evident from its low p_H and also from the fact that the ratio of the cupric-ion concentration to that of the total copper is smaller than the conductance ratio, α. The same is true of the copper malonate solution. Metallic bases that precipitate from still more acidic solutions become increasingly unable to react with the first stage and fail completely with the second stage.

Those bases which form "soluble basic salts" (Britton, J., 1925, **127**, 2120) behave mainly as very weak bases. Examples are beryllium and chromium hydroxide, and their inability to react seems to be related to the fact that 1 equiv. of each of the bases is only able to enter into a loose kind of combination with strong acids. Towards weak acids, this capacity to combine appears to be non-existent. As Table I shows, those products of the little combination that occurs possess low conductivities, for the conductivities of the solutions arise largely from the uncombined acid. As already expressed by Britton (*loc. cit.*), these bases are probably held in solution in a pseudo-colloidal form. This view has been contested by Sidgwick and Lewis (J., 1926, **1287**, 2540) on the grounds that basic beryllium salt solutions have not the ordinary properties of colloidal solutions. Moreover, they contend that McBain's views on colloidal electrolytes cannot apply to beryllium malonate solutions, because the viscosities and conductivities are small, and they therefore suggest that beryllium hydroxide must be held in the solutions in a non-polar cyclic form, $Be{<}^{O—CO}_{O—CO}{>}CH_2$, and that the abnormal constancy of conductivity on dilution is due to the ionisation $2BeM = Be^{\cdot\cdot} + [BeM_2]''$, the complex anion containing the stable 4-covalent beryllium. Such an hypothesis is not in accord with the low p_H value, 3·57, of 0·02M-beryllium malonate, which shows that the solution contains a relatively large proportion of hydromalonate to malonate ions, and that more than one-quarter of the very small conductivity is to be attributed to the hydrolysed acid.

A view more in harmony with the observations is to regard the hydrogen malonates as tending to correspond with the normal salts of strong acids and to undergo hydrolysis in the case of weak and very weak bases (*e.g.*, copper and aluminium hydroxides, respectively), *e.g.*, $Cu(HM)_2 + 2xH_2O = xCu(OH)_2 + (1 - x) Cu(HM)_2 + 2xH_2M$. The normal malonates hydrolyse in the first place in accordance with the scheme $2H_2O + 2CuM \rightleftharpoons Cu(HM)_2 + Cu(OH)_2$, the hydrogen malonate then hydrolysing still further as shown above. Support for this hypothesis is to be found in the fact that copper malonate solutions are saturated, or nearly so, with respect to copper hydroxide, inasmuch as their ionic products, $[Cu^{\cdot\cdot}][OH']^2$, are comparable with its solubility product. It is probable that some of the copper hydroxide is associated in solution with the hydrogen malonate, thus forming aggregates of basic copper hydrogen malonate which are feebly ionised and are maintained in solution in a highly dispersed state owing to their tendency to ionise (cf. the "solution link" of Thomas and Frieden, *J. Amer. Chem. Soc.*, 1923, **45**, 2522).

Ives and Riley (J., 1931, 1998) observed that the conductance ratios of the malonates and numerous alkylmalonates become smaller in passing through the series magnesium, zinc, nickel, copper. They attempted to explain this, but without success, on the basis of Riley's electronic hypothesis of localised ionic charges; and considered that the greater ionisation of zinc than of copper malonate must be regarded as an anomaly in view of the relative positions of the two metals in the periodic system.

It happens, however, that the order found by Ives and Riley is also that of the precipitation p_H's of the respective bases, that of copper hydroxide being the lowest. Such p_H values impose a limit upon the extent to which a weak acid may react in forming a normal soluble salt. The foregoing work shows that *normal* combination with the first stage of malonic acid is only possible when the precipitation p_H is higher than $p_{K_1} + 2$, and with the second stage when it is higher than $p_{K_2} + 2$. Malonates of such weak bases, however, can be isolated in crystalline form from acid solutions, but on dissolution in water much hydrolysis occurs in which the second stage of ionisation is largely involved.

Ives and Riley regard it as "highly significant" that the secondary dissociation con-

stants of diethyl- and dipropyl-malonic acids (Gane and Ingold, J., 1929, 1691) should be so very much smaller than that of malonic acid or of the other substituted acids of the series. They state that the failure of these constants to affect the dissociation of the malonato-cupriate complex ion is probably the result of the formation of a complete electron grouping round the central copper ion. The fact is that copper hydroxide is much too weak a base to react normally with the second stage of any of these acids, and consequently, it could scarcely be considered that any variation in the already small secondary dissociation constants would be perceptible.

In conclusion, the above work shows that any theory which purports to account for the relatively low dissociation of the salts formed from weak acids and heavy-metal bases must incorporate the dissociation constants of the acids and the strength of the base— the precipitation p_H of the base probably being the closest approach yet possible to the measure of the basic strength. Until these factors have been considered, it is premature to ascribe differences to the localisation of ionic charges, which in the case of salts studied by Riley is without any experimental support.

40. 3 : 6-*Dimethyl Glucose.*

By D. J. BELL.

AN addition compound of glucose with two molecules of metaboric acid has been utilised by Brigl and Grüner (*Annalen*, 1932, **495**, 60) for the preparation of 2 : 6-dibenzoylglucose. The possibility occurred to the author that similar treatment of the α- and the β-methyl-glucoside might produce 2 : 6-derivatives. The reactions indeed led to the formation of substances, having the composition of methylglucoside dimetaboric acid, which, when methylated in dry acetone, yielded about 50% of the original methylglucosides as the dimethyl derivatives. As these would not crystallise, they were benzoylated (compare Oldham, *J. Amer. Chem. Soc.*, 1934, **56**, 1360). The α-compound yielded no crystalline derivative and was not further investigated. A crystalline derivative obtained from the dimethyl β-methylglucoside (the yield, however, indicated that the original dimethyl derivative was a mixture of isomerides) was identified as 2 : 4-dibenzoyl 3 : 6-dimethyl β-methylglucoside by conversion into the 2 : 4-di-*p*-toluenesulphonate recently synthesised by Oldham (unpublished work). Debenzoylation of the crystalline dibenzoate gave a syrupy 3 : 6-*dimethyl β-methylglucoside*, and hydrolysis of the glucosidic methoxyl group yielded crystalline 3 : 6-*dimethyl glucose*. This compound shows downward mutarotation in water and therefore has the α-configuration.

That the 2 : 6-derivative was present in the mixture of dimethyl β-methylglucosides was shown in the following manner. Debenzoylation, followed by toluenesulphonation, of the syrupy residues after the crystallisation of 2 : 4-dibenzoyl 3 : 6-dimethyl β-methyl-glucoside gave a crystalline product, from which on fractionation 3 : 4-di-*p*-toluenesulphonyl 2 : 6-dimethyl β-methylglucoside, identical with the synthetic product of Oldham and Rutherford (*J. Amer. Chem. Soc.*, 1932, **54**, 1086), was isolated.

The above results show that the dimetaboric acid complexes are not homogeneous with respect to structure. It was also observed that only one molecule of the acid could be titrated with alkali in the presence of glycerol.

EXPERIMENTAL.

Condensation of α- *and* β-*Methylglucoside with Metaboric Acid.*—10 G. of the glucoside and 4·8 g. (2 mols.) of metaboric acid (both finely powdered and dried in a vacuum over phosphoric oxide) were boiled on the water-bath for 3 hours with 100 ml. of dry acetone : only a trace

remained undissolved. When dry benzene was added to the filtered liquid, a crystalline precipitate formed; this was washed with dry benzene and dry acetone and dried in a vacuum desiccator. The α-*derivative* had $[\alpha]_D^{16°} + 84\cdot4°$, and the β-*derivative* $- 60\cdot4°$, in acetone (*c*, 3·2) [Found for the α-derivative: OMe, 10·9; HBO_2 (by titration), 16·1. Found for the β-derivative: OMe, 10·7; HBO_2, 16·0. $C_7H_{14}O_6,2HBO_2$ requires OMe, 11·0; HBO_2, 31·2%].

Methylation of the β-Derivative.—This could be carried out either on the isolated boric acid derivative or with the original reaction mixture. The proportions employed, per mol. of the β-derivative, were acetone, 16 mols., silver oxide, 4 mols., methyl iodide, 6 mols., and the duration of heating at 35° was 6 hours. (Modification of these conditions, or further methylation of the isolated product, did not improve the yield.) After methylation, the solution was filtered and evaporated to dryness, the residue dissolved in potassium carbonate solution, and the dimethyl methylglucoside separated from higher and lower homologues by the author's usual procedure (*Biochem. J.*, 1932, **26**, 590). The yield was one-half to one-third of the weight of the β-derivative (only very small amounts of mono- and tri-methyl glucosides were formed). The product had the composition of a dimethyl methylhexoside, distilled at 150°/0·4 mm. without residue, but would not crystallise.

2 : 4-Dibenzoyl 3 : 6-Dimethyl β-Methylglucoside.—The mixed glucosides described above were benzoylated in pyridine for 24 hours (100% excess of benzoyl chloride gave the best yield). The product was washed and dried (over sodium sulphate) in ether, and light petroleum (b. p. 40—60°) added until a permanent turbidity was produced. Hard needles were deposited on scratching, and the filtrate gave a second crop on repetition of this treatment. Recrystallisation from methyl alcohol raised the m. p. to 155—156°. Yield, 25%, $[\alpha]_D^{19°}$ (chloroform) $- 11\cdot65°$ (*l* = 2, *c* = 3·0) (Found: C, 64·3; H, 6·1; OMe, 21·85. Calc. for $C_{23}H_{26}O_8$: C, 64·2; H, 6·05; OMe, 21·65%).

3 : 6-Dimethyl β-Methylglucoside.—2·0 G. of the preceding compound, debenzoylated by Oldham's method (*loc. cit.*), gave 0·9 g. (yield, 90%) of a colourless syrup having $[\alpha]_D^{16°} + 55\cdot4°$ in methyl alcohol and $+ 62\cdot9°$ in chloroform (*c* = 3·5, *l* = 2) (Found: OMe, 41·8. $C_9H_{18}O_6$ requires OMe, 41·9%).

2 : 4-Di-p-toluenesulphonyl 3 : 6-Dimethyl β-Methylglucoside.—3 : 6-Dimethyl β-methylglucoside (0·67 g.) was treated with *p*-toluenesulphonyl chloride (1·54 g.; 4 mols.) in the minimum of pyridine for 3 days at 25°. After the usual procedure a crystalline residue was obtained from the evaporated benzene solution. Recrystallised from ethyl alcohol (yield, 93%), the crystals melted at 158—160°, had $[\alpha]_D^{15°}$ (chloroform) $- 22\cdot8°$ (*c* = 4·5, *l* = 2), and did not depress the m. p. of synthetic 2 : 4-di-*p*-toluenesulphonyl 3 : 6-dimethyl β-methylglucoside (m. p. 158—160°, $[\alpha]_D^{15°} - 22\cdot8°$).

3 : 6-Dimethyl α-Glucose.—The preceding glucoside, in 5% concentration, was heated at 100° in 5% hydrochloric acid until the rotation attained a constant value (4 hours). After neutralisation of the acid with silver carbonate, removal of colloidal silver with norite, and evaporation of the solution to dryness in a vacuum, the sugar was obtained as a straw-coloured glass. The dried product was dissolved in pure ethyl acetate and decolorised with a little norite; from the solution, concentrated somewhat, the sugar was deposited in hard lumps of stout needles, m. p. 113—116° (Found: C, 46·0; H, 7·6; OMe, 30·1. $C_8H_{16}O_6$ requires C, 46·2; H, 7·7; OMe, 29·8%). $[\alpha]_D^{16°}$ in water: initial value $+ 102\cdot5°$, falling to $+ 61\cdot52°$.

In water (*c* = 3·316, *l* = 2).

Time (mins.)	0	5	15	30	45	17 (hrs.)
$\alpha_D^{15°}$	$+ 6\cdot88°$ (by extrapolation)	6·23°	5·54°	4·92°	4·65°	4·08° (const.)

Isolation of the Toluenesulphonyl Derivative of 2 : 6-Dimethyl β-Methylglucoside.—The syrupy residues remaining from the crystallisation of 2 : 4-dibenzoyl 3 : 6-dimethyl β-methylglucoside were debenzoylated and treated with *p*-toluenesulphonyl chloride in the usual manner. The crude crystalline product, m. p. 135—141°, on fractional crystallisation from ethyl alcohol, gave a middle fraction, m. p. 156—158°, which melted at 156—158° when mixed with authentic ditoluenesulphonyl 2 : 6-dimethyl β-methylglucoside, but at 140—152° in admixture with the 3 : 6-dimethyl derivative.

41. *Polysaccharides. Part XIX. The Molecular Structure of Waxy Maize Starch.*

By W. N. Haworth, E. L. Hirst, and (Mrs.) M. Dorothea Woolgar.

On the basis of previous work the hypothesis we have advanced in this series of papers is that the two main constituents of starch represent physical units having a greater or lesser degree of aggregation of the primal chemical unit. The latter we recognise as a continuous chain terminating after a length of 26—30 α-glucopyranose units has been attained. These two main constituents of starch have been variously described in the literature as amylopectin and amylose (Maquenne and Roux, *Compt. rend.*, 1903, **137**, 88) and as α-amylose and β-amylose respectively (A. Meyer, *Ber. deut. bot. Ges.*, 1886, **4**, 337; " Untersuchungen über die Stärkekörner," 1895). In our discussion of this subject we have preferred to use the nomenclature of Maquenne and Roux, and to avoid confusion it should be pointed out that the alternative nomenclature employing the terms α- and β-amylose has no essential connexion with a stereochemical difference of the units composing the starch constituents.

It was obviously desirable to examine the chain length of the chemical molecule of a variety of starch differing as widely as possible from that which we had already examined. In the endosperm of a number of cereals a so-called red-staining starch has been encountered. It occurs in *Oryza sativa* var. *glutinosa*, *Panicum miliaceum* var. *canditum glutinosum*, *Sorghum vulgare glutinosum*, and in another variety of grass, *Coix lachryma-jobi*. The most readily available source of a starch of this character is, however, waxy maize, of which we have been able to obtain a supply through the courtesy of Professor R. A. Brink, Department of Genetics, Wisconsin University, to whom we express our thanks (compare R. A. Brink and F. A. Abegg, *Genetics*, 1926, **11**, 163). This variety of starch is characterised by giving a red-violet coloration with iodine, not unlike the red-brown colour given by glycogen but differing very markedly from the deep blue colour given by potato starch or ordinary maize starch. It has already been suggested that the red and blue colours given by different starches or their analogues are due to differences in the degree of dispersion of the iodine particles and that any agency such as alcohol, potassium iodide, or heat which has the effect of bringing the iodine into true solution tends to change the colour in the direction of blue to red. For this reason it is suggested by Brink that the ultimate particles of waxy maize starch may be smaller than those of the non-waxy type, thus permitting of a greater surface on which the iodine is distributed. Beyond surmise, little can be gained from our present knowledge of colour reactions. Certainly it is the case that in waxy maize starch the amylose (β-amylose) portion greatly preponderates. It forms viscous solutions with water rather than pastes, and differs materially in general properties from starches in which a high proportion of amylopectin (α-amylose) is present.

From waxy maize starch we have prepared the acetate by two methods involving respectively pyridine and a mixture of sulphur dioxide and chlorine as catalytic agents. The starch regenerated from the acetate retained the same properties as the original starch and, moreover, the acetates prepared by the two methods were indistinguishable. From the two acetates we have also prepared the corresponding fully methylated derivatives. These have closely similar properties, but differ somewhat from each other in their specific viscosities in *m*-cresol. Methylated waxy maize starch resembled in all respects the methylated amylose fraction of potato starch described in two preceding papers (Haworth, Hirst, and Webb, J., 1928, 2581; Hirst, Plant, and Wilkinson, J., 1932, 2375). The methylated starches showed no variation in optical rotation from the previous specimens and the magnitude of the rotation was in agreement with the additive rule of Freudenberg (*Ber.*, 1933, **66**, 177) for continuous units of methylated α-glucopyranose.

The gravimetric assay of the end group isolated by hydrolysis of methylated waxy maize starch revealed the presence of an average of 4·5% of tetramethyl glucose, which corresponds to a chain length of 26—30 α-glucopyranose units. This value, which was found with both specimens of waxy maize starch referred to above, irrespective of their

viscosity, is similar to that which we have already determined for methylated amylose and methylated amylopectin from potato starch, and it is interesting to record that two starches of such different origins give results corresponding to the same value. The apparent molecular weight determined by the viscosity method, using Staudinger's factor, gives values many times greater than that found by the gravimetric assay, and this is also the case when the sedimentation method with the ultra-centrifuge (Svedberg, *Ber.*, 1934, **67**, *A*, 117) is applied. On the basis of our theory of the constitution of starch it is clear that this specimen also was an amylose which owing to molecular aggregation is still much more complex than the limiting chemical molecule.

EXPERIMENTAL.

Preparation of Waxy Maize Starch.—Clean waxy maize grains were steeped in dilute sulphurous acid (*d* 1·007) for 24 hours at 40°. The softened grains were washed with water and pounded to a pulp under water. The pulp was enclosed in fine muslin and kneaded under water until all the starch had passed into the water. The aqueous suspension was poured through a fine sieve to remove any large particles and the starch was allowed to settle. After decantation of the supernatant liquid the crude starch was made into a flowing paste with water and poured slowly into *N*/10-aqueous sodium hydroxide. The mixture was stirred at intervals during 4 hours, the starch allowed to settle, washed with water, and again allowed to settle. The washing with water was repeated several times until all traces of alkali were removed. The starch was digested at 15° in succession with 95% alcohol, absolute alcohol, and ether. The starch thus prepared was a white impalpable powder which contained 6·8% of moisture. After the starch had been kept in the air for some time, the moisture content rose to 20%.

Properties of Waxy Maize Starch.—The granules of waxy maize starch appear under the microscope as small rounded discs with indentations at the circumference. The granules stain with iodine dark blue at the margin and reddish-purple in the interior. Waxy maize starch is not appreciably soluble in cold water, but dissolves readily in warm water (40—50°), giving an opalescent solution. This solution after cooling gives with iodine a reddish-purple colour which very slowly changes to blue. The colour disappears when the solution is heated and on subsequent cooling a deep green colour appears which changes gradually to an intense blue. Waxy maize starch prepared by the above method had no ash content and contained no nitrogen. The phosphorus content was very small (P, 0·0025%) (Found : C, 44·2; H, 6·4. Calc. for $C_6H_{10}O_5$: C, 44·4; H, 6·2%). The starch had no action on Fehling's solution on prolonged boiling, and its iodine number, determined by the method of Bergmann and Machemer, was negligible (0·4—0·6).

Waxy maize starch gave only moderately viscous solutions with warm water. The " pastes " so obtained were much less viscous than potato starch paste prepared in a similar way. For example, the times taken in a viscometer were respectively 28·2 seconds for potato starch paste and 10·8 seconds for waxy maize starch paste. In each case a 1% paste had cooled to 20°. At this temperature the time for water in the same instrument was 9 seconds.

Owing to the opalescence of the solutions determination of the rotation of waxy maize starch was difficult to carry out in water or sodium hydroxide. For this reason, " prepared " starch was used for the polarimetric measurements. " Prepared " starch was obtained by precipitating an aqueous solution of waxy maize starch with alcohol, grinding the precipitate under alcohol, washing it with ether, and drying it in a vacuum. The prepared starch differed from the original waxy maize starch in being immediately soluble in cold water. In all other respects its properties were identical with those recorded above. In particular it was non-reducing and had a negligible iodine number. Its aqueous solution gave a deep red-purple colour with iodine. $[\alpha]_{5780}^{20°} + 212°$ in water (*c*, 0·97); + 153° in 4% aqueous sodium hydroxide (*c*, 1·30).

Experiments carried out under strictly comparable conditions and with the same enzyme preparation showed that the rates of hydrolysis of waxy maize starch and potato starch with barley diastase were almost identical. After 4 hours at 50° both solutions showed reducing properties corresponding to 60% conversion into maltose. When the product was worked up in the usual way, crystalline maltose was obtained.

Attempts to separate waxy maize starch into fractions corresponding to amylose and amylopectin by Ling and Nanji's method were unsuccessful. The starch was made into a paste (1·5%) with water and frozen for 30 minutes in ice–salt. During the subsequent extractions with warm water the whole of the starch dissolved, except a small portion (less than

0·1% of the total) consisting mainly of inorganic material derived from the aluminium pans used during the freezing process. It appears, therefore, that waxy maize starch cannot be separated into fractions corresponding to the amylose and amylopectin portions of potato starch. It consists entirely of the more soluble form corresponding to amylose. The starch extracted by the warm water in the above experiments was precipitated by alcohol from the concentrated extract. It was ground under alcohol and washed with alcohol and then with ether. Its properties were identical with those of " prepared " starch (see above).

Acetylation of Waxy Maize Starch.—(a) A solution of the starch in hot water was poured, with brisk stirring, into an excess of alcohol. The precipitate was ground under alcohol to a fine powder, which was washed with ether and dried in a vacuum. This prepared starch (5 g.) was steeped in glacial acetic acid (30 c.c.) through which chlorine had been passed for 90 seconds. Acetic anhydride (50 c.c.) containing sulphur dioxide equivalent to the amount of chlorine was then added and the mixture was stirred for 1 hour at 20° and for 1 hour at 55°. The clear solution was filtered through glass wool and poured into a large volume of water. The white granular precipitate of acetylated waxy maize starch was washed with water until acid-free, then with alcohol and ether, and dried in a vacuum (yield, quantitative). The *acetyl* derivative was a crisp white powder readily soluble in acetone and in chloroform. It gave no colour with iodine and was non-reducing towards Fehling's solution. $[\alpha]_D^{22°}$ + 167° in chloroform (c, 0·3) (Found : C, 50·2; H, 5·8; CH_3·CO, 44·6. $C_{12}H_{16}O_8$ requires C, 50·0; H, 5·6; CH_3·CO, 44·6%). After systematic fractionation from chloroform solution by addition of light petroleum the main portion (88%) of the acetate was obtained as a white powder with the rotation and analytical figures given above and having $\eta_{sp.}$ 0·51 in *m*-cresol at 20° (c, 0·4%) (corresponding to an apparent molecular weight of 37,000 by Staudinger's formula). (The viscosity measurements given in this paper are recorded only for comparative purposes, since it cannot be assumed at this stage that the viscosities of these substances are utilisable directly for the calculation of molecular weights.)

(b) *With pyridine as catalyst.* Prepared starch (3 g.) was shaken for 2 hours with pyridine (30 c.c.). Acetic anhydride (30 c.c.) and pyridine (10 c.c.) were then added and the mixture was shaken for 3 hours. The clear solution was poured into a large excess of water and the starch triacetate was isolated in the usual way (yield, quantitative). The acetylated starch was identical in properties with that prepared by method (a). When heated, it began to sinter at about 180° and to decompose at about 210°. $[\alpha]_{5780}^{18°}$ + 166° in chloroform (c, 1·0). The phosphorus content of the original starch was retained during the acetylation (Found : C, 49·7; H, 5·8; CH_3·CO, 46·0; P, 0·0013%).

Fractional precipitation of the acetate from acetone solution by regulated addition of light petroleum disclosed the essential homogeneity of the material. Three fractions were obtained, all of which had the properties given above and were indistinguishable from one another as regards analytical figures. The specific viscosities of the fractions in solution in *m*-cresol were almost identical. $\eta_{sp.}$ 0·48 (c, 0·4%) in *m*-cresol at 20°, corresponding to an " apparent " molecular weight (Staudinger's formula) of 35,000.

Acetylation of the original starch either by Barnett's method or by the pyridine method proceeded less readily and was incomplete and the product was only partly soluble in acetone.

Regeneration of Waxy Maize Starch from the Acetate.—The finely powdered acetate (4 g.) (prepared by the pyridine method) was shaken for 30 minutes with 100 c.c. of 0·5N-alcoholic sodium hydroxide. The alkali was then neutralised with N-acetic acid and the solid was separated by filtration and ground under alcohol containing a little acetic acid. This treatment was repeated, the starch was then dissolved in warm water (40°), and the solution neutralised with acetic acid, filtered, and poured into alcohol. The precipitated starch was washed with alcohol and ether and dried in a vacuum (yield, 70%). Its properties were identical with those of the original starch in its " prepared " condition, *i.e.*, after precipitation from aqueous solution by alcohol. $[\alpha]_{5780}^{20°}$ + 152° in 4% aqueous sodium hydroxide (c, 0·5); + 180° in 0·4% aqueous sodium hydroxide; + 214° in water (c, 0·1). It was soluble in cold water, it had no action on boiling Fehling's solution, and its iodine number was negligible (< 2). Like the original starch, it gave with iodine a reddish-purple colour, which disappeared on heating. On subsequent cooling, a green-blue colour, changing to a permanent blue, was observed. The viscosities of aqueous solutions of the regenerated and the original material were identical. The phosphorus content was also similar to that of the original starch (0·003%). No appreciable difference was found between the original and the regenerated waxy maize starch.

Simultaneous Deacetylation and Methylation of Waxy Maize Starch Acetate.—The acetate (in lots of 15 g.), dissolved in acetone (200 c.c.), was methylated at 55° by methyl sulphate

(180 c.c.) and 30% aqueous sodium hydroxide (600 c.c.), the reagents being added slowly with vigorous stirring. The methylation was facilitated by addition of acetone (200 c.c. in all) to replace losses by evaporation. At the end of the reaction hot water was added (400 c.c.) and the temperature was raised to 100°. After 30 minutes the methylated product was separated, washed with boiling water, dissolved in acetone, and remethylated. The yield was then 90% of the theoretical, and the methoxyl content 39%. $[\alpha]_D$ + 195° in chloroform. After six further methylations the methoxyl content had risen to 43%. The methylated starch was then dissolved in chloroform to remove insoluble inorganic impurities and was obtained as a brittle sponge-like mass on evaporation of the chloroform. Acetone condensation products were removed by extraction with boiling ether, leaving the methylated starch as a pale yellow, granular solid, which was soluble in chloroform and acetone, only very slightly soluble in ether, and insoluble in alcohol and in hot water. In cold water swelling took place and the substance became glutinous. It was non-reducing and gave no colour with iodine; m. p. 146°; $[\alpha]_D^{20°}$ + 206° in chloroform (c, 0·6) (Found : OMe, 43·4%).

Fractionation of Methylated Waxy Maize Starch.—The methylated starch (16 g.), dissolved in chloroform (30 c.c.), was fractionally precipitated by addition of light petroleum (b. p. 40—60°). After systematic treatment involving re-fractionation from chloroform–ether, three principal fractions were obtained : Fraction (a), 0·6 g., m. p. 126—140°, was slightly discoloured and contained a small amount of acetone condensation products which had escaped removal by the previous ether extraction of the methylated starch. Fraction (b), 10·2 g., m. p. 156° with previous softening, $[\alpha]_D^{20°}$ + 206° in chloroform (c, 0·8), was further fractionated, giving three portions which had exactly similar properties, including specific viscosity in m-cresol solution; m. p. 153—156° with previous softening; $[\alpha]_D^{20°}$ + 206° in chloroform; $\eta_{sp.}$ 0·40 (c, 0·30%) in m-cresol at 20°, corresponding to an apparent molecular weight (Staudinger's formula) of 27,000 : the method of purification and the fractionation ensured that this material was free from ash and from traces of decomposition products [Found : C, 52·4; H, 8·1; OMe, 43·4. $C_9H_{16}O_5$ requires C, 52·9; H, 7·8; OMe, 45·6%. Methylated starch (OMe, 43·4%) requires C, 52·5; H, 7·7%]. Fraction (c), 3·8 g., m. p. 160° after previous softening, $[\alpha]_D$ + 194° in chloroform (c, 0·62) (Found : OMe, 39%), contained some ash (5%) and consisted mainly of incompletely methylated material.

Hydrolysis of Methylated Waxy Maize Starch.—Freshly powdered methylated starch (fraction b, 9·5 g.) was dissolved by stirring in ice-cold fuming hydrochloric acid (53 c.c.). The solution was saturated with hydrogen chloride at − 15° and left for 24 hours, first in a freezing mixture (ice–salt) and then at 0°. The excess of hydrogen chloride was removed by aëration at 15°, the solution diluted with water (60 c.c.), and the acid neutralised with barium carbonate at 15°. After filtration the solution was evaporated to dryness at 40°/12 mm. The solid residue was extracted with boiling chloroform. The material (9·0 g.) extracted by the chloroform was boiled for 7 hours with 3% methyl-alcoholic hydrogen chloride. The product (8·7 g.), which was isolated in the usual way, had $n_D^{18°}$ 1·4602. On fractional distillation a portion (A) (4·0 g.) was obtained, b. p. 136—145°/0·027 mm. (bath temp.). The first drop of distillate had $n_D^{18°}$ 1·4451, and the last drop $n_D^{18°}$ 1·4580. No tetramethyl methylglucoside remained in the still residue. Fractionation of (A) from a Widmer flask gave (B) (0·47 g.), b. p. 144°/0·03 mm. (bath temp.), $n_D^{18°}$ 1·4472 (first drop, $n_D^{18°}$ 1·4455; last drop, $n_D^{18°}$ 1·4530) (Found : OMe, 58·0%). On the basis of refractive index and methoxyl content, (B) contained 70% by weight of tetramethyl methylglucoside. This was confirmed by hydrolysis of the distillate with boiling 5% hydrochloric acid, which gave crystalline tetramethyl glucose in good yield. After (B) had been collected, another fraction (C) (0·91 g.) was obtained, b. p. 150—158°/0·03 mm., $n_D^{18°}$ 1·4552 (first drop, $n_D^{18°}$ 1·4537; last drop, 1·4557) (Found : OMe, 52·9%). This fraction contained at most 0·1 g. of tetramethyl methylglucoside. Further distillation of (A) gave pure trimethyl methylglucoside, $n_D^{18°}$ 1·4570. The total yield of tetramethyl methylglucoside was therefore 0·43 g. This requires a correction of 10% to allow for losses during manipulation (see Haworth and Machemer, J., 1932, 2270). The final yield was therefore 0·47 g. This corresponds to a yield of 4·7% of tetramethyl glucose from methylated waxy maize starch. The identity of the trimethyl methylglucoside was confirmed by its hydrolysis to crystalline 2 : 3 : 6-trimethyl glucose.

Methylated Waxy Maize Starch from the Acetate prepared with Sulphur Dioxide and Chlorine as Catalyst.—The acetate (the main portion obtained during fractionation) was methylated by the method described above. After five methylations the rotation of the product was $[\alpha]_D^{20°}$ + 211° in chloroform and the methoxyl content was 42·3%. After 6 further methylations the product was purified by washing with boiling water and after being dried was extracted

five times with boiling ether to remove acetone condensation products. The last ethereal extracts contained only a trace of material, which appeared to be methylated starch having OMe, 44·2%. The main portion of the methylated waxy maize starch was a pale yellow powder, soluble in chloroform and acetone, insoluble in alcohol and in boiling water, slightly soluble in ether. In cold water it became glutinous (yield, 85%). Fractional precipitation from chloroform solution by addition of light petroleum separated the methylated product into three main fractions : (A), 5% of the total, $\eta_{sp.}$ 0·02; (B), 12% of the total, $\eta_{sp.}$ 0·06; (C), 80% of the total, $\eta_{sp.}$ 0·12 (apparent mol. wt.—see above—approx. 6000). The viscosities in each case refer to solutions in *m*-cresol at 20° containing 0·04 g. in 10 c.c. Each fraction had OMe 44—45%, and $[\alpha]_D^{20°}$ + 204° in chloroform. Attempts to separate (C) into further fractions were unsuccessful [Found for (C) : C, 52·8; H, 8·0%].

Fraction (C) (15 g.) was hydrolysed by boiling 1% methyl-alcoholic hydrogen chloride (600 c.c.). The reaction was complete in 4 hours. The acid was neutralised with silver carbonate, and the products (15·7 g.) were isolated in the usual way and submitted to fractional distillation under diminished pressure. The first portion (6·3 g., bath temp. 125—130°/0·03 mm.) was refractionated from a Widmer flask, giving (a) 0·7 g. (bath temp. 135—144°/0·03 mm.), $n_D^{18°}$ 1·4470 (Found : OMe, 59·6%). This fraction consisted, to the extent of 80%, of tetramethyl methylglucopyranoside. After hydrolysis with 3% hydrochloric acid, tetramethyl glucopyranose was obtained in good yield. (b) 0·2 G. (bath temp. 150°/0·03 mm.), $n_D^{18°}$ 1·4535. (c) Pure 2 : 3 : 6-trimethyl methylglucoside, which crystallised in the receiver : the crystalline β-form had m. p. 57°, $[\alpha]_D^{18°}$ — 32° in water (*c*, 0·3), after recrystallisation from light petroleum. The non-crystalline portion had $n_D^{20°}$ 1·4553 (Found : OMe, 52·0%), and both this and the crystalline substance gave in excellent yield on hydrolysis 2 : 3 : 6-trimethyl glucose, m. p. 117° alone or when mixed with an authentic sample. After removal of all the trimethyl methylglucoside by distillation a fraction (0·4 g.) was obtained, b. p. 225°/0·02 mm., $n_D^{21°}$ 1·4685 (Found : OMe, 46·3%). This contained some dimethyl methylglucoside. There remained an undistillable residue (2 g.) which was not further examined.

From the above figures the corrected yield of tetramethyl methylglucoside from 15 g. of methylated starch was 0·66 g., corresponding to an estimated chain length of 29 units.
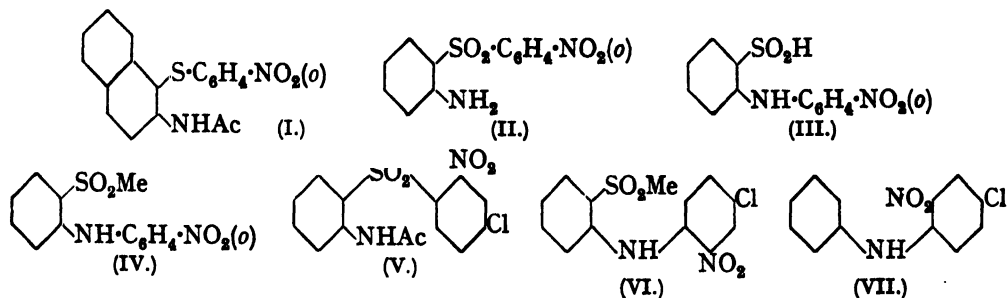
42. *A Rearrangement of* o-*Acetamido-sulphones and -sulphides.*

By WILFRID J. EVANS and SAMUEL SMILES.

DURING a study of the rearrangement of *o*-amino-sulphones it was shown (J., 1932, 2774) that the acetamido-derivatives of one of these (I, S replaced by SO_2) suffered rearrangement without deacetylation. In this case the process evidently consists in a displacement of sulphonyl by the acetamido-group and is analogous with that observed (J., 1933, 1490) with *o*-acetamido-sulphoxides in which the thionyl group is similarly displaced. Two further examples of this rearrangement have been examined. The sulphone (II) with aqueous sodium hydroxide easily gave the sulphinic acid (III). This was characterised as a sulphinic acid by conversion into a disulphide and the methyl-sulphone (IV); further proof of its structure was obtained by removal of the sulphinic group. With sulphinic acids derived from diphenyl ether the degradation has been effected (J., 1931, 3267) by oxidation, followed by hydrolysis of the sulphonic acid in acid media; but with the diphenylamine derivatives now in question this process was unsuccessful. A better method and one which is recommended for general use in the degradation of aromatic sulphinic acids was found in their reaction with mercuric chloride, which removed sulphur dioxide and yielded the mercurichloride, Ar·HgCl (Peters, *Ber.*, 1905, 38, 2567; Kharasch and Chalkley, *J. Amer. Chem. Soc.*, 1921, 43, 607); the metal was then removed from the latter by hydrochloric acid. By this treatment the sulphinic acid (III) yielded 2-nitrodiphenylamine.

The acetyl derivative of (II) with one molecular proportion of alkali hydroxide gave the acetyl derivative of (III); this was characterised by methylation, which yielded the acetyl derivative of (IV), the relationship of this to (IV) being established by hydrolysis.

N

Similarly, the sulphone (V) with excess of alkali hydroxide yielded a sulphinic acid (compare III), which gave a methyl-sulphone (VI) and a disulphide and was converted into (VII) by the method of degradation described. The same sulphone (V) with one molecular proportion of alkali hydroxide was converted into the acetyl derivative of a sulphinic acid (compare III) and thence into the acetylated methyl-sulphone (compare VI), which yielded (VI) on hydrolysis. The methyl-sulphones (IV) and (VI) have served as standards in determining the structure of the products obtained by rearrangement of *o*-acetamido-sulphoxides (J., 1933, 1490).

The results of these experiments and others preceding them (J., 1932, 2774; 1933, 1490) have now given several examples in each case of the rearrangement of *o*-amino-sulphones, *o*-acetamido-sulphones, and *o*-acetamido-sulphoxides; it is now evident in substances of this type, which contain the sulphur group attached to positive carbon, that sulphonyl may be displaced by aromatic amino- and acetamido-groups, and thionyl by the acetamido-group. A survey of the rearrangements which have been encountered (summary on p. 184) in the experiments arising from the conversion of *iso*-2-naphthol sulphide into 2-naphthol 1-sulphide shows not only that they may be referred to the same general type (VIII ⟶ IX), but also that the conditions controlling them are similar.

In the case of the 2-hydroxy-sulphones (VIII; X = SO_2, YH = OH) it has been shown (J., 1934, 422) that, apart from the stereochemical relationship of X and Y to c, the chief factors to be considered are (1) the positive character of c, (2) the capacity of Y to meet the electron demand at c, and (3) the tendency of YH to lose a proton in the medium employed. Comparing the behaviour of a series in which c was provided by an *o*-nitro-group, it was found that, when YH was aromatic hydroxyl, rearrangement took place when X was SO_2 but not with X as SO or S; and when YH was aliphatic hydroxyl, that X might be SO_2 or SO, but with S as X rearrangement did not take place. These relations indicate that the character of X must be regarded as a fourth condition determining this type of rearrangement and, as might be expected, that with a given YH and c a decrease in the positive
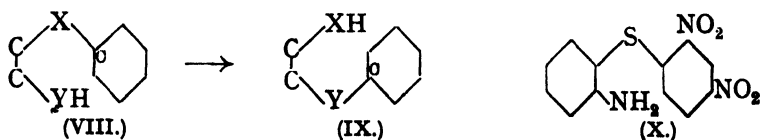
character or increase in the negative character of X is less favourable to the displacement of the latter. This view is confirmed by the behaviour of the corresponding amino-derivatives. Whilst the amino-sulphones of this series (VIII; X = SO_2, YH = NH_2) readily undergo rearrangement in presence of warm alkali hydroxide, the relevant *o*-amino-sulphides (I, NHAc replaced by NH_2), (II, SO_2 replaced by S), (V, NHAc replaced by NH_2, and SO_2 by S), (X), and (XI) are unattacked even by alcoholic sodium hydroxide. The acetyl derivative of (XI) was obtained together with oxidation products by nitrating the acetyl derivative of (II); the given structure is assigned to it because after deamination 2 : 4'-dinitrodiphenyl sulphide was obtained, and the corresponding acetylated sulphone, after rearrangement and degradation of the sulphinic acid formed, yielded 2 : 3'-dinitro-diphenylamine. The method used (J., 1934, 422) with the *o*-hydroxy-sulphones for investi-

gating the influence of changes in the character of YH (VIII) cannot be applied to the *o*-amino-sulphones; nevertheless, interesting results have been obtained by a qualitative examination of suitable derivatives. For the present purpose the character of the amino-group (YH) was more effectively varied by substitution in the group itself than by substitution in the aromatic nucleus bearing it.
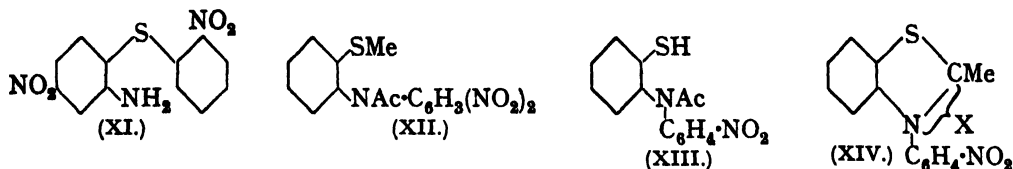
The derivatives of the sulphone (II) in which YH is NHMe, NH$_2$, NHAc, or NH·SO$_2$Ph form a series in which the donor capacity of the nitrogen diminishes (condition 2) and its tendency to lose a proton increases (condition 3). All these derivatives undergo rearrangement, yielding the corresponding diphenylamine-2-sulphinates. Attention is directed to the requirement of concentrated alkali to effect the rapid change of the methylamino-sulphone (J., 1932, 2774) and to the incomplete conversion of the benzenesulphonyl derivative under usual conditions. The former circumstance may be regarded as due to the reluctance of the methylamino-group to lose a proton, and the latter to the feebler electron supply offered by the nitrogen.

Turning to the *o*-amino-sulphides, it was found, in contrast with the inactivity of the parent amines, that the acetyl derivatives of all these suffered rearrangement in alcoholic sodium hydroxide. The products, evidently the *N*-acetylthiols (compare XIII), were not in all cases isolated, but were obtained after methylation as the methylthiols (*e.g.*, XII); these gave methyl mercaptan with hydriodic acid and in the cases of the sulphides (I), (II, SO$_2$ replaced by S, and NH$_2$ by NHAc), (V, SO$_2$ replaced by S), and (XI, NH$_2$ replaced by NHAc) were identified after oxidation by comparison with the corresponding derivatives (*e.g.*, IV) obtained from the sulphones through the sulphinic acids. The methylthiol (XII), obtained from the acetyl derivative of (X), was hydrolysed; the product was identical with that furnished by synthesis from 2-aminothioanisole and 1-chloro-2 : 4-dinitrobenzene.

The *N*-acetylthiols (*e.g.*, XIII) behave as pseudo-bases (compare Mills, Clark, and Aeschliman, J., 1923, 2353) and are converted by acids into salts to which the structure (XIV) may be provisionally assigned; the investigation of the latter substances is being continued. The salts in question are also formed by reduction of the *N*-acetyl-sulphinic acids (compare III, where NH is NAc) with hydriodic acid. This noteworthy difference in behaviour of the 2-amino-sulphides and their acetyl derivatives is ascribed to the amino-group acquiring by acetylation an increased tendency to lose a proton; at the same time it is evident that acetylation has not depressed the donor function of the nitrogen sufficiently to prevent that element meeting the demand of the positive carbon atom concerned. It is worth notice that the conversion of the nitro-derivative (XI, NH$_2$ replaced by NHAc) was remarkably quicker than that of the parent sulphide (II; SO$_2$ replaced by S, and NH$_2$ by NHAc); this may be attributed mainly to weakening of the negative character of the thio-group by nitration in the para-position.

The explanation given to the behaviour of these *N*-acetyl derivatives leads to the conclusion that the rearrangement of the *N*-substituted 2-amino-sulphides of this type depends for its success on the proper balance of these two essential properties of the nitrogen group (VIII; YH = NRH, X = S). In an extreme case where the donor capacity of Y in YH is high, the tendency to proton release would be slight and the rearrangement might then fail under mildly alkaline conditions. On the other hand, when a proton is easily set free from YH, and Y may form an ion in the medium used, the rearrangement might fail owing to the diminished electron supply available from Y. The series of *N*-substituted sulphones gave, as already described, indication that these conditions might be attained in cases where X (VIII) is less positive than sulphonyl and therefore less easily displaced. Accordingly the following series of *N*-substituted derivatives of 2'-nitro-2-aminodiphenyl sulphide was

examined; the results agree with those anticipated : NMe_2, NHMe, NH_2, NHAc, $NH \cdot CO \cdot C_6H_4 \cdot NO_2(o)$, $NH \cdot C_6H_2(NO_2)_3$, $NH \cdot SO_2Ph$.

In hot alcoholic sodium hydroxide (1 mol., $N/3$), only the acetyl and the 2-nitro-benzoyl derivatives suffered rearrangement; the picryl and the benzenesulphonyl derivatives yielded sodium salts and were recovered from these. The case of the 2-nitro-benzoyl derivative is worth attention; rearrangement of this substance proceeds far less readily than that of the acetyl derivative; in fact under the usual conditions the greater part of the material was recovered and only a small amount of the product of rearrangement, about 20%, could be isolated as the *S*-methyl ether (compare XII). The accord of theory with this behaviour is evident.

Further support is thus obtained for the views expressed concerning the general character of these rearrangements and the conditions which govern them.

Since the discovery of the conditions attending the conversion of *iso*-2-naphthol sulphide into 2-naphthol sulphide was made (J., 1931, 914) eight varieties of the general type of rearrangement (VIII ——→ IX) have been encountered. These are summarised by the following list, which shows in the case of each YH the groups capable of playing the part of X in the rearrangements hitherto observed. All the rearrangements indicated have been observed with c (VIII) furnished by an *o*-nitro-group as well as in many other cases with c more, or less, positive than this. The list also shows the influence of varying YH and X on the occurrence of rearrangement : it is obviously capable of extension; *e.g.*, the rearrangement

If YH is NHAc,   X may be SO_2, SO, or S.

   „ „ OH (Al.),   „ „ SO_2, SO, but not S.

   „ „ NH_2(Ar.),   „ „ SO_2, (SO ?), but not S.

   „ „ OH (Ar.),   „ „ SO_2, but not SO or S.

   „ „ SH,   „ „ O.

of *o*-thiol-sulphones may be expected, and this conclusion is supported by the recent observation of a corresponding intermolecular displacement (Cowie and Gibson, J., 1934, 47). At the present state of the investigation it may be stated in general terms that re-arrangement of (VIII) may take place if Y in the substituent YH is able more fully to satisfy the demand at c than X and also is able under the conditions of experiment to lose a proton for the requirement of X. With regard to the mechanism of the process it is suggested, in accord with the view of Bennett and Chapman (*Ann. Reports*, 1930, 122), that the interaction of c and Y establishes a preliminary phase (compare also Baddeley and Bennett, J., 1933, 261), such as (XV), leading to the liberation of the proton from YH. The behaviour of the *o*-hydroxy-sulphones (J., 1931, 3266) indicates that, if c is ortho or para to a nitro-group, an unstable nitronic ion such as (XVI) is formed before final release of X from c takes place.

(XV.) $\bar{N}O_2$ (XVI.)
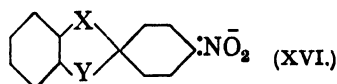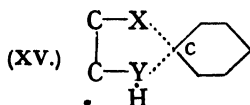
EXPERIMENTAL.

Derivatives of 2-*Aminodiphenyl Sulphide.*—(a) 2-Nitro-2′-aminodiphenyl sulphide (J., 1933, 1492) gave an *acetyl* derivative, which formed yellow needles from alcohol, m. p. 138° (Found : C, 58·1; H, 4·4. $C_{14}H_{12}O_3N_2S$ requires C, 58·3; H, 4·2%), and a *benzenesulphonyl* derivative, forming needles from benzene, m. p. 172° (Found : C, 55·9; H, 3·8; N, 7·5. $C_{18}H_{14}O_4N_2S_2$ requires C, 56·0; H, 3·6; N, 7·3%). The *o-nitrobenzoyl* derivative was obtained from the amine by interaction with *o*-nitrobenzoyl chloride in acetone solution in presence of sodium carbonate; it had m. p. 150° and formed yellow needles from acetic acid (Found : C, 57·6; H, 3·5; N, 10·8. $C_{19}H_{13}O_5N_3S$ requires C, 57·7; H, 3·3; N, 10·6%). Picryl chloride and the amine in alcohol with sodium acetate gave the *picryl* derivative, which formed red prisms from acetic acid, m. p. 206—207° (Found : N, 15·6. $C_{18}H_{11}O_8N_5S$ requires N, 15·3%).

2-*Nitro*-2′-*methylaminodiphenyl sulphide* was obtained by boiling (2 hours) a solution of the above amino-sulphide (4 g.) in alcohol (10 c.c.) which contained methyl iodide (2 c.c.) and mag-

nesium oxide (0·6 g.). It formed orange prisms from alcohol, m. p. 110° (Found : C, 59·8; H, 4·7; N, 10·7; S, 12·0. $C_{13}H_{12}O_4N_2S$ requires C, 60·0; H, 4·6; N, 10·8; S, 12·3%), and was recovered from boiling (3 hours) alcohol containing sodium hydroxide ($N/2$). The *acetyl* derivative formed yellow plates from alcohol, m. p. 124° (Found : C, 59·8; H, 4·8; N, 9·3. $C_{15}H_{14}O_5N_2S$ requires C, 59·6; H, 4·6; N, 9·3%). The o-*nitrobenzoyl* derivative had m. p. 146° and formed yellow needles from alcohol (Found : C, 58·5; H, 3·9; N, 10·4. $C_{20}H_{15}O_5N_3S$ requires C, 58·7; H, 3·7; N, 10·3%).

2-*Nitro*-2′-*dimethylamino*-5′-*methyldiphenyl sulphide* separated when a solution of 2-nitro-phenylchlorothiol (14 g.) and dimethyl-*p*-toluidine (28 g.) in ether was boiled (1·5 hours); it formed yellow prisms, m. p. 104° (Found : C, 62·5; H, 5·8; N, 10·0. $C_{15}H_{16}O_2N_2S$ requires C, 62·5; H, 5·5; N, 9·7%), which were unaltered by boiling $N/2$-alcoholic sodium hydroxide (3 hours).

(b) 2 : 4′-*Dinitro*-2′-*acetamidodiphenyl sulphide* (compare XI). When the acetyl derivative (5 g.) of the amino-sulphide (a) was added (15°) to stirred nitric acid (25 c.c., d 1·4), it dissolved and subsequently the required *product* separated in the crystalline state (35%). It formed yellow plates from acetic acid, m. p. 179—180° (Found : C, 50·4; H, 3·4; N, 12·9. $C_{14}H_{11}O_5N_3S$ requires C, 50·5; H, 3·3; N, 12·6%). When it was heated (100°, 1·5 hours) with sulphuric acid (60%), it was converted into 2 : 4′-*dinitro*-2′-*aminodiphenyl sulphide* (XI), which separated when the liquid was diluted. The amine formed yellow plates, m. p. 193° (Found : C, 49·3; H, 3·3. $C_{12}H_9O_4N_3S$ requires C, 49·5; H, 3·1%). The substance was recovered after its solution in $N/2$-alcoholic sodium hydroxide had been boiled (3 hours). It was deaminated by addition of cuprous oxide to a solution of the diazonium sulphate in alcohol. When decomposition was complete, cuprous oxide was removed; the required product separated from the cooled solution. It crystallised from alcohol in yellow plates, m. p. 158°, identical with a specimen of 2 : 4′-*dinitrodiphenyl sulphide* prepared by boiling (2 hours) a solution of *p*-chloronitrobenzene (13 g.) and sodium *o*-nitrophenyl mercaptide (20 g.) in alcohol (50 c.c.). The product contained *o*-nitrophenyl disulphide, which was removed by treatment in warm alcohol with glucose and sodium hydroxide; the residue (9 g.) was washed and purified from acetic acid; m. p. 158—159° (Found : C, 52·4; H, 2·8. $C_{12}H_8O_4N_2S$ requires C, 52·2; H, 2·9%).

(c) 4-Chloro-2-nitro-2′-aminodiphenyl sulphide and its acetyl derivative have been previously described (J., 1933, 1492).

(d) 2 : 4-*Dinitro*-2′-*aminodiphenyl sulphide* (X), obtained from sodium 2-aminophenyl mercaptide and 2 : 4-dinitrochlorobenzene by a process similar to that used in the cases of sul-phides (a) and (c), separated from acetic acid in deep yellow needles, m. p. 148° (Found : C, 49·3; H, 3·1; N, 14·5. $C_{12}H_9O_4N_3S$ requires C, 49·5; H, 3·1; N, 14·4%). The *acetyl* derivative had m. p. 199° (Found : N, 12·8; S, 9·7. $C_{14}H_{11}O_5N_3S$ requires N, 12·6; S, 9·6%).

(e) *o*-Nitrophenyl 2-acetamido-1-naphthyl sulphide (I) was prepared by Zincke's method (*Annalen,* 1912, 391, 82).

Derivatives of 2-*Aminodiphenylsulphone.*—(a) 2-*Nitro*-2′-*acetamidodiphenylsulphone.* A solution of the corresponding sulphide (2 g.) in acetic acid (20 c.c.) containing hydrogen peroxide (3 c.c., 30%) was kept at 100° (1 hour). The required *sulphone* (1·9 g.) separated when the cooled mixture was diluted; it formed needles from alcohol, m. p. 107° (Found : C, 52·4; H, 3·9; N, 9·1. $C_{14}H_{12}O_5N_2S$ requires C, 52·5; H, 3·8; N, 8·8%). The use of a larger excess of hydrogen peroxide in this process gave 2 : 2′-dinitrodiphenyl sulphide, m. p. 183°, as the chief product.

(b) 2-*Nitro*-2′-*aminodiphenylsulphone* was formed by hydrolysis of the acetamido-sulphone (a) (10 g.) with sulphuric acid (60%) at 100° (1 hour) and was isolated (7·8 g.) by dilution of the cold mixture. It formed prisms from alcohol, m. p. 132—134° (Found : C, 51·7; H, 4·1; N, 10·4; S, 11·7. $C_{12}H_{10}O_4N_2S$ requires C, 51·8; H, 3·6; N, 10·1; S, 11·5%).

(c) 4-*Chloro*-2-*nitro*-2′-*acetamidodiphenylsulphone.* A solution of the corresponding sulphide (2 g.) in acetic acid (20 c.c.) containing hydrogen peroxide (2·3 c.c., 30%) was kept at 100° (1 hour). The product, isolated in the usual way, formed needles, m. p. 171°, from alcohol (Found : C, 47·2; H, 3·4. $C_{14}H_{11}O_5N_2ClS$ requires C, 47·4; H, 3·1%).

(d) 2-*Nitro*-2′-*benzenesulphonamidodiphenylsulphone.* The sulphide (5 g.) slowly dissolved in hot (100°) acetic acid (30 c.c.) when "hyperol" (5·2 g.) was gradually added to the mixture; the required *sulphone* (4·4 g.) separated when the solution was subsequently (1 hour) cooled. It formed needles from acetic acid, m. p. 144—145° (Found : C, 51·6; H, 3·5. $C_{18}H_{14}O_6N_2S_2$ requires C, 51·7; H, 3·3%).

(e) When the preceding sulphone was methylated with methyl sulphate in presence of aqueous alkali, 2-*nitro*-2′-*benzenesulphonylmethylaminodiphenylsulphone* separated as an oil,

which solidified in contact with alcohol and was purified from acetic acid; m. p. 189° (Found : C, 52·5; H, 3·5. $C_{16}H_{16}O_6N_2S_2$ requires C, 52·8; H, 3·7%).

(f) 2 : 4'-*Dinitro*-2'-*acetaminodiphenylsulphone*. A mixture of acetic acid (20 c.c.) containing hydrogen peroxide (2·5 c.c., 30%) and the acetamido-sulphide (b) (2 g.) was kept at 100° (1·5 hours) and then diluted. The impure material which separated was re-oxidised (1·2 c.c., 30% H_2O_2) under the same conditions. When the mixture was cooled, the required *sulphone* separated; it formed pale yellow prisms, m. p. 186—187° (Found : C, 45·7; H, 3·4. $C_{14}H_{11}O_7N_3S$ requires C, 46·0; H, 3·0%).

Attempts to convert the picryl derivative of sulphide (a) into the sulphone by the usual method yielded 2-*nitro*-2'-*picrylamidodiphenyl sulphoxide*, which formed pale yellow needles, m. p. 250—251° (decomp.) Found : N, 15·0. $C_{18}H_{11}O_9N_5S$ requires N, 14·8%).

Rearrangement of Sulphones.—The sulphone (a) gradually (30 mins.) dissolved in hot (100°) *N*-sodium hydroxide (2·5 mols.). When the red solution had been cooled and acidified with dilute sulphuric acid, 2-o-*nitrophenylaminobenzenesulphinic acid* (III) was liberated; it formed orange plates from acetic acid, m. p. 124° (Found : C, 51·7; H, 3·8. $C_{12}H_{10}O_4N_2S$ requires C, 51·8; H, 3·6%). Bis-2-o-nitrophenylaminophenyl disulphide separated when hydriodic acid (*d* 1·7) was added to a solution of this sulphinic acid in warm acetone containing sulphur dioxide; it formed orange plates from acetic acid, m. p. 149—150° (Found : C, 58·7; H, 3·4; N, 11·7. Calc. : C, 58·8; H, 3·7; N, 11·4%), and was identical with the disulphide (J., 1933, 1493) isolated from the product of rearrangement of the sulphoxide. Interaction of methyl iodide and the sodium sulphinate yielded 2-o-nitrophenylaminophenylmethylsulphone, m. p. 132° (Found : C, 53·3; H, 4·4. Calc. : C, 53·4; H, 4·1%), identical with the product obtained by oxidising the methyl sulphoxide (*loc. cit.*). When a boiling solution of the sulphinate, obtained as described from the sulphone (a) by rearrangement, was added to a hot solution of mercuric chloride (1·8 g.) in water (6 c.c.), sulphur dioxide was liberated. Subsequently (30 mins.) the impure mercurichloride was collected, washed with water, and treated (1·5 hours) with a boiling mixture of alcohol (10 c.c.) and concentrated hydrochloric acid (10 c.c.). The oil which separated from the mixture solidified when it was cooled; the product after purification (0·6 g.) from alcohol had m. p. 76° and was identical with a synthetic sample of 2-nitrodiphenylamine. The acetamido-sulphone (a) was also submitted to the action of 1 mol. of aqueous-alcoholic sodium hydroxide (*N*/2). When the boiling solution had become neutral, methyl iodide was added; finally the solvent was evaporated and the product which separated from the residue was purified from alcohol, 2-*aceto*-o-*nitrophenylamidophenylmethylsulphone* (compare IV) being obtained, m. p. 135—136° (Found : C, 53·4; H, 4·4; S, 9·4. $C_{15}H_{14}O_5N_2S$ requires C, 53·8; H, 4·2; S, 9·6%) : this was converted by hydrolysis with alcoholic sodium hydroxide into the methyl-sulphone (IV). The amino-sulphone (b) yielded in presence of boiling *N*-sodium hydroxide (1 mol.) a solution of the sodium sulphinate (III). This product was identified by conversion into the disulphide and the methyl-sulphone (IV) described above.

The acetamido-sulphone (c, V) rapidly dissolved (5 mins.) in boiling *N*-sodium hydroxide (2·5 mols.) ; the sulphinic acid, liberated from the cooled solution, was not purified, but converted into bis-2-p-*chloro*-o-*nitrophenylaminophenyl disulphide*, which formed orange plates from acetic acid, m. p. 174° (Found : C, 51·7; N, 10·0; S, 11·5. $C_{24}H_{16}O_4N_4Cl_2S_2$ requires C, 51·5; N, 10·0; S, 11·5%). Methylation of the sulphinic acid in alkaline solution yielded 2-p-*chloro*-o-*nitrophenylaminophenylmethylsulphone* (VI), which separated from propyl alcohol in orange plates, m. p. 190° (Found : C, 47·5; H, 3·5; S, 9·8; Cl, 10·8. $C_{13}H_{11}O_4N_2ClS$ requires C, 47·8; H, 3·4; S, 9·8; Cl, 10·9%). Degradation of the sulphinic acid by the usual method gave 4-chloro-2-nitrodiphenylamine (VII), which was identified by comparison with a synthetical specimen.

2-*Aceto*-p-*chloro*-o-*nitrophenylamidophenylmethylsulphone*. Alcohol containing sodium hydroxide (1 mol., *N*/4) and the acetamido-sulphone (c) was boiled (30 mins.) until the solution had become neutral. After addition of methyl iodide and further boiling, the solution was cooled; the required *methyl-sulphone* then separated, m. p. 172° (Found : C, 48·8; H, 3·2. $C_{15}H_{13}O_5N_2ClS$ requires C, 48·8; H, 3·5%), and was converted by alkaline hydrolysis into the methyl-sulphone (VI).

A solution of the sulphone (d) in aqueous alcohol (50%) containing sodium hydroxide (1·25 mols., 0·5*N*) was boiled (2 hours). Methylation of the solution thus obtained yielded 2-o-*nitrophenylbenzenesulphonamidophenylmethylsulphone*, which formed plates, m. p. 169° (Found : C, 52·7; H, 4·0. $C_{19}H_{16}O_6N_2S_2$ requires C, 52·8; H, 3·7%), and was different from the sulphone (e).

A hot aqueous solution of the sodium sulphinate formed by rearrangement of the sulphone (d) yielded with mercuric chloride sulphur dioxide and a mercurichloride which was not attacked

by hydrochloric acid under the usual conditions. This substance, evidently 2-o-*nitrophenyl-benzenesulphonamidophenyl mercurichloride*, formed needles from acetone, m. p. 224—225° (Found : C, 36·7; H, 2·5. $C_{18}H_{12}O_4N_2ClSHg$ requires C, 36·7; H, 2·2%).

The sulphone (f) was rapidly attacked (10 mins.) by sodium hydroxide (1 mol.) in boiling alcohol. Methylation of the product yielded 5-*nitro*-2-*aceto*-o-*nitrophenylamidophenylmethyl-sulphone*, m. p. 175—176° (Found : C, 47·1; H, 3·7; N, 11·2. $C_{15}H_{13}O_7N_3S$ requires C, 47·5; H, 3·4; N, 11·1%). With 2 mols. of sodium hydroxide the sulphone (f) yielded a sulphinic acid, from which by degradation 2 : 3'-*dinitrodiphenylamine* was obtained. This formed orange needles, m. p. 158° (Found : N, 16·1. $C_{12}H_9O_4N_3$ requires N, 16·2%), which were different from 2 : 4-dinitrodiphenylamine (m. p. 156°) and identical with the product obtained by heating (190°, 4 hours) a mixture of m-nitroaniline (3 g.), o-bromonitrobenzene (5 g.), sodium carbonate (1·5 g.), and cuprous bromide (0·1 g.).

Rearrangement of Sulphides.—A solution of the acetyl derivative of the sulphide (a) (2 g.) in a mixture (50%) of acetone and alcohol which contained sodium hydroxide (1·25 mols., $N/2$) was boiled (15 mins.); when excess of methyl iodide was added to the solution, the red colour faded and after most of the solvent had been evaporated the methylthiol (1·4 g.) separated. 2-*Aceto*-o-*nitrophenylamidophenyl methyl sulphide* formed yellow needles, m. p. 151° (Found : C, 59·6; H, 4·9; N, 9·4; S, 10·6. $C_{15}H_{14}O_3N_2S$ requires C, 59·6; H, 4·6; N, 9·3; S, 10·6%), which gave methyl mercaptan with hot hydriodic acid and on oxidation yielded the methyl-sulphone obtained by rearrangement of the acetamido-sulphone (a). Hydrolysis of the substance with alcoholic sodium hydroxide gave 2-o-*nitrophenylaminophenyl methyl sulphide*, which formed red needles from alcohol, m. p. 98° (Found : C, 59·9; H, 4·6; N, 10·9; S, 12·2. $C_{13}H_{12}O_2N_2S$ requires C, 60·0; H, 4·6; N, 10·8; S, 12·3%). Oxidation of this substance yielded the methyl-sulphone obtained by methylation of the sulphinic acid related to the sulphone (b) by rearrangement.

2-*Aceto*-o-*nitrophenylamidophenyl mercaptan* was isolated by rearrangement of the sulphide (a) in acetone as described. After the solvent had been removed, water was added and the clear solution of the sodium salt was acidified with dilute sulphuric acid. The product separated from alcohol in yellow needles, m. p. 114° (Found : C, 58·2; H, 4·5; M, 286. $C_{14}H_{12}O_3N_2S$ requires C, 58·3; H, 4·2%; M, 288).

2-o-*Nitrophenyl*-1-*methylbenzthiazolonium iodide* (XIV) was obtained from this thiol by addition of hydrogen iodide to an acetone solution; it formed yellow plates, m. p. 203° (decomp.) (Found : C, 42·0; N, 7·1. $C_{14}H_{11}O_2N_2IS$ requires C, 42·2; N, 7·0%). The same substance was obtained from the corresponding sulphinic acid by reduction with hydriodic and sulphurous acids; it was decomposed by warm water, yielding hydriodic acid and a red material which was not further investigated. The *perchlorate*, obtained from the thiol with perchloric acid, had m. p. 192° (Found : N, 7·7. $C_{14}H_{11}O_6N_2ClS$ requires N, 7·6%).

Rearrangement of the sulphide (c) was effected in boiling alcoholic sodium hydroxide (1·25 mols., $N/2$) as in the case of (a). After methylation, 2-*aceto*-p-*chloro*-o-*nitrophenylamidophenyl methyl sulphide* separated from the cooled mixture; it formed yellow plates, m. p. 142° (Found : C, 53·7; H, 4·1; S, 9·4. $C_{15}H_{13}O_3N_2ClS$ requires C, 53·5; H, 3·9; S, 9·5%), and on oxidation yielded the methyl-sulphone which had been obtained by rearrangement of the sulphone (c).

2-p-*Chloro*-o-*nitrophenylaminophenyl methyl sulphide*, obtained from the above acetyl derivative by hydrolysis in an alkaline medium, formed red needles from acetic acid, m. p. 126° (Found : C, 53·0; H, 4·0. $C_{13}H_{11}O_2N_2ClS$ requires C, 53·0; H, 3·1%). It yielded methyl mercaptan with hydrogen iodide and was converted by oxidation into the methyl-sulphone (VI).

Rearrangement of the sulphide (d) was effected as in the cases of (a) and (c). Since the product of rearrangement underwent further change in presence of warm alkali solution, it was isolated as the methylthiol. 2-*Aceto*-op-*dinitrophenylamidophenyl methyl sulphide* (XII) was obtained by the gradual addition of methyl iodide during the process (15 mins.). It separated from the cooled reaction mixture and formed yellow needles from acetic acid, m. p. 155—156° (Found : C, 51·5; H, 3·9; N, 12·3; S, 8·9. $C_{15}H_{13}O_5N_3S$ requires C, 51·9; H, 3·7; N, 12·1; S, 9·2%). By deacetylation with hot (100°) dilute sulphuric acid (60%) it was converted into 2-op-dinitrophenylaminophenyl methyl sulphide identical with a specimen prepared by Zincke's method (*Ber.*, 1915, 48, 1242) from o-aminothioanisole and 2 : 4-dinitrochlorobenzene.

Rearrangement of the sulphide (e) was effected in a boiling acetone-alcohol solution of sodium hydroxide (1·25 mols., $N/3$), the alkaline reagent being gradually added as the change progressed. When methyl iodide was added to the boiling solution, the colour rapidly faded and after removal of most of the solvent and addition of water the required product separated.

2-*Aceto*-o-*nitrophenylamido*-1-*naphthyl methyl sulphide* formed yellow needles from alcohol,

m. p. 158° (Found : C, 64·8; H, 4·8. $C_{19}H_{16}O_8N_2S$ requires C, 64·8; H, 4·5%). The substance yielded methyl mercaptan with warm hydriodic acid and was converted by oxidation into the 2-aceto-*o*-nitrophenylamido-1-naphthylmethylsulphone (m. p. 195°) previously (J., 1932, 2777) obtained by rearrangement of the sulphone. Alkaline deacetylation of the substance gave 2-*o*-*nitrophenylamino*-1-*naphthyl methyl sulphide*, which formed bright red plates from alcohol, m. p. 110° (Found : C, 65·8; N, 9·3. $C_{17}H_{14}O_2N_2S$ requires C, 65·8; N, 9·0%). Rearrangement of the sulphide (e) in acetone without concurrent methylation gave a solution of the sodium salt of the thiol; this was isolated by acidification of the clear diluted solution and was converted by hydrogen iodide in acetic acid into 2-*o*-nitrophenyl-1-methylnaphtha-thiazolonium tri-iodide, m. p. 183°, which had been previously (*loc. cit.*) obtained by reduction of the sulphinic acid.

Rearrangement of the *N*-*o*-nitrobenzoyl derivative (8 g.) of the sulphide (a) was effected in acetone–alcohol (*N*/2-sodium hydroxide, 1·25 mols.) and required longer (1·5 hours) treatment than usual. Gradual methylation was begun during the latter part of the process; most of the required product separated when the liquid was cooled; a further quantity was subsequently obtained from the solution (yield, 1·8 g.). 2-*o*-*Nitrobenzo*-*o*-*nitrophenylamidophenyl methyl sulphide* formed pale yellow needles, m. p. 245° (Found : C, 58·7; N, 10·3. $C_{20}H_{15}O_5N_3S$ requires C, 58·7; N, 10·3%); it yielded methyl mercaptan with hydriodic acid and was different from the *N*-methyl derivative of the sulphide from which it was prepared.

Rearrangement of the sulphide (b) (1 g.) was rapidly effected (15 mins.) as usual (1 mol. sodium hydroxide, *N*/3) in boiling acetone–alcohol. After methylation of the product in the solution, most of the solvent was evaporated; the methylthiol (0·9 g.) then separated. Obtained in this way, 5-*nitro*-2-*aceto*-*o*-*nitrophenylamidophenyl methyl sulphide* formed prisms from acetic acid, m. p. 192—193° (Found : C, 51·7; N, 12·3. $C_{15}H_{13}O_5N_3S$ requires C, 51·9; N, 12·1%), which gave methyl mercaptan as usual and yielded after oxidation a methyl-sulphone (m. p. 176°) identical with that obtained by rearrangement of the sulphone (f).

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43. *Reactions of Methyl Δ^β-Propene-αaβ-tricarboxylate. An Example of Three-carbon Ring-chain Prototropy involving a Simple cycloPropane Ring.*
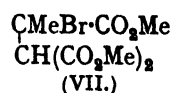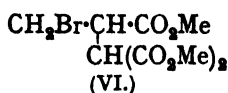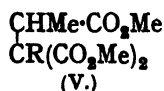
By JOHN W. BAKER.

ALTHOUGH an unequivocal example of three-carbon ring-chain prototropy involving the formation of a *cyclo*butane ring is provided by the self-condensation of various glutaconic esters (Ingold, Perren, and Thorpe, J., 1922, **121**, 1765), no conclusive evidence has hitherto been obtained for the simplest case involving the reversible formation of a *cyclo*propane ring (cf. Baker, J., 1925, **127**, 985, 1682). Evidence has now been obtained of the reversible interconversion of the open-chain propene ester (II) and its cyclic tautomeride (IV), in which the *cyclo*propane ring is presumably stabilised by the spatial effect of the carbomethoxy-groups, which will also greatly increase the ionisability of the mobile hydrogen and confer high mobility on the electromeric system involved. Interconversion presumably occurs through the mesomeric ion (III), which must possess a high degree of degeneracy.

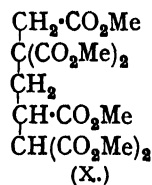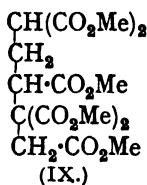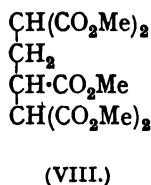(I.)   (II.)   (III.)   (IV.)
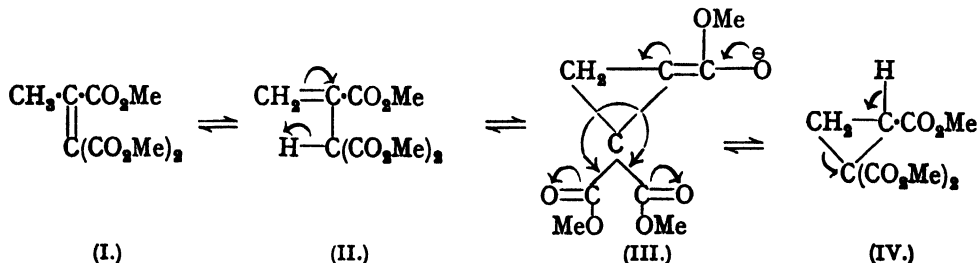
It has already been noted (J., 1934, 1467) that methyl Δ^β-propene-αaβ-tricarboxylate (II) is the main product of the action of warm pyridine on methyl α-bromo-*n*-propane-

$\alpha\alpha\beta$-tricarboxylate (V, R = Br), the Δ^α-ester (I), which is presumably the initial product, undergoing prototropic change into the Δ^β-ester, which, on the basis of the known effect of a β-carbomethoxy-substituent (Shoppee, J., 1930, 968), would be expected to be the more stable open-chain form.

CHMe·CO₂Me	CH₂Br·CH·CO₂Me	CMeBr·CO₂Me
CR(CO₂Me)₂	CH(CO₂Me)₂	CH(CO₂Me)₂
(V.)	(VI.)	(VII.)

ĊHMe·CO₂Me
ĊR(CO₂Me)₂
(V.)

ĊH₂Br·ĊH·CO₂Me
ĊH(CO₂Me)₂
(VI.)

ĊMeBr·CO₂Me
ĊH(CO₂Me)₂
(VII.)

There can be little doubt as to the structure of the original α-bromo-ester (V, R = Br), since this is obtained by direct bromination of the malonyl hydrogen in the parent saturated ester (V, R = H) (Baker, J., 1933, 811). Moreover, reduction of the α-bromo-ester regenerates the original saturated parent. The presence of a methylene group in the Δ^β-ester (II) is proved by the production of formaldehyde upon ozonolysis, further confirmation of its constitution being provided by the structure of the product obtained by addition of hydrogen bromide. The solid bromo-ester, m. p. 70°, so obtained is methyl γ-bromo-n-propane-$\alpha\alpha\beta$-tricarboxylate (VI) (J., 1934, 1467), since it condenses with methyl sodiomalonate to give, not methyl β-methyl-n-propane-$\alpha\alpha\beta\gamma\gamma$-pentacarboxylate as previously supposed (J., 1933, 811), but *methyl n-butane-$\alpha\alpha\beta\delta\delta$-pentacarboxylate* (VIII), which is hydrolysed by boiling concentrated hydrochloric acid to n-butane-$\alpha\beta\delta$-tricarboxylic acid identical with a specimen obtained by similar hydrolysis of ethyl n-butane-$\alpha\beta\beta\delta$-tetracarboxylate (Kay and Perkin, J., 1906, 89, 1642).

ĊH(CO₂Me)₂
ĊH₂
ĊH·CO₂Me
ĊH(CO₂Me)₂
(VIII.)

ĊH(CO₂Me)₂
ĊH₂
ĊH·CO₂Me
Ċ(CO₂Me)₂
CH₂·CO₂Me
(IX.)

ĊH₂·CO₂Me
Ċ(CO₂Me)₂
ĊH₂
ĊH·CO₂Me
ĊH(CO₂Me)₂
(X.)

The formation of the γ-bromo-ester (VI) can be satisfactorily explained only if the unsaturated ester has the structure (II).

Evidence of the prototropic interconversion of the Δ^α- and the Δ^β-ester was forthcoming by re-examination of the products obtained by the addition of hydrogen bromide to the unsaturated ester. When contact with the hydrogen bromide (in acetic acid) was prolonged (10 days), or when the unsaturated ester, recovered as a by-pre?... in the preparation of (VIII) by condensation of the γ-bromo-ester (VI) with methyl sodiomalonate, was employed, the resultant crude solid bromo-ester had a much lower m. p. (45°) than that usually observed, and fractional crystallisation from ligroin separated it into the less soluble γ-bromo-ester (VI), m. p. 70°, and a small amount of a very soluble, isomeric bromo-ester, m. p. 54°, which must be *methyl β-bromo-n-propane-$\alpha\alpha\beta$-tricarboxylate* (VII). The two bromo-esters cannot be dimorphous forms, since they could not be interconverted and, moreover, in one crystallisation the two very distinctive types of crystal (clusters of fine needles, m. p. 64—65°, and large stout prisms, m. p. 52—54°, respectively) were obtained side by side; they were mechanically separated, and depressed each other's melting point to 45°. There is, of course, the possibility that the β-bromo-ester (VII) is derived from the Δ^β-ester (II) by a reverse hydrogen bromide addition, but this explanation is rendered highly improbable by the fact that, when the pure Δ^β-ester (below) was employed, *only* the γ-bromo-ester could be isolated. The β-bromo-ester is therefore almost certainly obtained by normal addition of hydrogen bromide to the Δ^α-ester (I) present in the equilibrium mixture of Δ^α- and Δ^β-esters resulting from the catalytic action of pyridine or sodium methoxide respectively. The direct action of methyl-alcoholic sodium methoxide on the Δ^β-ester is referred to later. The isolated observation (J., 1933, 814) that mesaconic acid was obtained by hydrolysis of the parent unsaturated ester with methyl-alcoholic potassium hydroxide is readily understood in the light of the results of Linstead and Mann (J., 1931, 726) concerning the position of equilibrium attained in the propene-$\alpha\beta$-dicarboxylic acids

(70% mesaconic acid) in the presence of hot alkali. Hydrolysis with boiling concentrated hydrochloric acid affords itaconic acid.

In order to obtain a pure specimen of the Δᵝ-ester, the original unsaturated ester was converted into its sodium derivative in dry ether, and this was decomposed by a slight deficiency of benzoic acid (Kon and Watson, J., 1932, 1). The resulting Δᵝ-ester, b. p. 139°/1·9 mm., exhibits no essential change in properties. It gives formaldehyde on ozonolysis, but with hydrogen bromide affords *only* the γ-bromo-ester.

Evidence of its tautomeric interconversion into the *cyclo*propane ester (IV) is provided by the formation of *cyclo*propane-1 : 1 : 2-tricarboxylic acid when the Δᵝ-ester is hydrolysed with concentrated methyl-alcoholic potassium hydroxide. Incidentally the same acid is also obtained (possibly by direct elimination of hydrogen bromide) when the γ-bromo-ester is similarly hydrolysed, a reaction which further confirms the structure assigned to the latter ester. There is, of course, a possible alternative explanation to ring-chain prototropic change for the production of the *cyclo*propane acid from the Δᵝ-propene ester, *viz.*, the intermediate formation of the γ-methoxy-ester, which then undergoes ring-closure with fission of methyl alcohol. Unfortunately, such an explanation cannot be definitely excluded, since attempts to prepare the methoxy-ester, by the action either of silver acetate and methyl alcohol, or of dry sodium methoxide (1 mol.) in dry ether, on the γ-bromo-ester (VI) resulted in the formation of methyl *cyclo*propane-1 : 1 : 2-tricarboxylate.

When, however, ethyl *cyclo*propane-1 : 1 : 2-tricarboxylate (Conrad and Guthzeit, *Ber.*, 1884, **17**, 1186), which, as expected, is saturated to potassium permanganate and gives no formaldehyde upon ozonolysis, is submitted to short treatment with boiling methyl-alcoholic sodium methoxide, the recovered ester contains unsaturated material and, on ozonolysis, formaldehyde is readily isolated as its dimedon compound. The most feasible explanation of this observation is a ring-chain prototropic change catalysed by alkoxide ion, the only alternative explanation being the rather distasteful hypothesis of addition and subsequent fission of methyl alcohol (in a different direction) during the one experimental process.

When the Δᵝ-unsaturated ester (II) is treated with N-methyl-alcoholic sodium methoxide (1 mol.), the main initial reaction is a Michael condensation affording the unsaturated dimeric ester (XI), which then undergoes a further internal Michael reaction to give saturated *methyl* cyclo*hexane*-1 : 1 : 2 : 4 : 4 : 5-*hexacarboxylate* (XII) : this is isolated as one of the main products of the reaction. Hydrolysis affords cyclo*hexane*-1 : 2 : 4 : 5-*tetracarboxylic acid*, dehydrogenated by selenium to pyromellitic acid.

$$(X = CO_2Me)$$
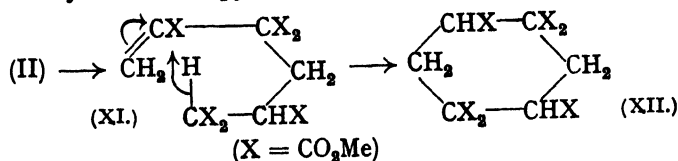
The actual isolation of the unsaturated ester (XI) has not been achieved. Treatment of the unsaturated gum [from which the crystalline ester (XII) had separated] with hydrogen bromide in acetic acid afforded the bromo-ester (VI) [from unchanged (II)] and a (?) *stereoisomeride* of the saturated ester (XII).

Thus, under the influence of alkali the Δᵝ-propene ester (II) may undergo either a reversible intramolecular Michael change to give the *cyclo*propane ester (IV) (ring-chain tautomerism), or an intermolecular condensation to afford the dimeric ester (XI), in which a further internal Michael condensation then takes place. A quantitative examination of the triple tautomeric system, (I) ⇌ (II) ⇌ (IV), would therefore probably be complicated and has not yet been attempted, but the results obtained suggest that the proportion of (I) present at equilibrium is very small, and that the equilibrium is located mainly in the direction of (IV).

The structure (VIII) which it is now necessary to assign to the condensation product of the γ-bromo-ester and methyl sodiomalonate means that the synthesis of esters of the type $CHX_2 \cdot CMeX \cdot CHX_2$ (*loc. cit.*) still remains unachieved, and the ester (VIII) is, of course,

valueless as an intermediate in the synthesis of the bile acid degradation product $C_{13}H_{20}O_6$. Before the true constitution of (VIII) had been established, however, several successive steps in the synthesis had been carried out. Condensation of the sodium derivative of (VIII) with methyl iodoacetate affords (probably) *methyl n-pentane-$\alpha\beta\beta\gamma\epsilon\epsilon$-hexacarboxylate* (IX), although the alternative structure (X), involving condensation with the other malonic residue of (VIII), cannot be excluded. Hydrolysis of (IX) affords a n-*pentane-tetracarboxylic acid* ($\alpha\beta\gamma\epsilon$- or $\alpha\beta\delta\epsilon$-), the *methyl* ester of which undergoes a Dieckmann reaction to give a *methyl* cyclo*hexanonetricarboxylate* (2 : 3 : 4-, 2 : 4 : 5-, or 2 : 3 : 5-).

<div align="center">EXPERIMENTAL.*</div>

Methyl Δ^β-Propene-$\alpha\alpha\beta$-tricarboxylate (II) (813).—This ester and not the Δ^α-ester appears to be the main product of the action of pyridine on methyl α-bromo-*n*-propane-$\alpha\alpha\beta$-tricarboxylate. The bromo-ester (50 g.) was added to 30 g. of pyridine; the mixture was gently warmed on the steam-bath for $\frac{1}{4}$ hour, left at room temperature for 24 hours, and again warmed for $\frac{1}{4}$ hour. After cooling, it was largely diluted with dry ether, the precipitated pyridine hydrobromide filtered off and washed with dry ether, and the combined filtrates, after removal of ether, fractionally distilled under reduced pressure. After distillation of the excess of pyridine, the unsaturated ester (25 g.) distilled at 150°/15 mm. A few grams of unchanged bromo-ester were recovered, b. p. *ca.* 160°/7 mm. This procedure eliminates the successive treatment with pyridine previously found to be necessary. To obtain the pure Δ^β-ester, 1·5 g. of sodium dissolved in 10—15 c.c. of dry methyl alcohol were evaporated to dryness in a vacuum, the residual sodium methoxide was evaporated three times with dry ether, and 10·8 g. of the " recovered " unsaturated ester in 50 c.c. of ether were added. Addition of 75 c.c. of ligroin (b. p. 60—80°) precipitated the slightly sticky sodium derivative, which was shaken with 6 g. of benzoic acid (theory, 6·1 g.) for 18 hours. The liquid was filtered, the solvent evaporated, and the residue distilled. After about 3 g. had been collected at 130—135°/2·5 mm., 5·5 g. of the Δ^β-*ester* distilled at 132°/1·9 mm.

Ozonolysis. Essentially similar results were obtained by ozonolysis of all specimens of the unsaturated ester in hexane solution for 48 hours. After evaporation of the solvent at room temperature in a vacuum, the ozonide was decomposed with cold water, with addition of dilute sodium hydrogen carbonate solution to neutralise the acid formed. The neutral product was extracted with ether and obtained as a colourless syrup. Since in no case did the product give a colour with ferric chloride, this neutral product is probably a mixture of further degradation products of the primary product, methyl oxalylmalonate, but none of these could be definitely identified. With semicarbazide acetate, only minute yields of semicarbazones, too small for identification, were obtained. Distillation of the aqueous sodium hydrogen carbonate solution gave formaldehyde, isolated as its dimedon compound, m. p. and mixed m. p. 189—190°. From the undistilled aqueous liquor, after evaporation to dryness and acidification with cold concentrated hydrochloric acid, was isolated a brown syrup, from which some oxalic acid dihydrate, m. p. 99°, raised to 102° by admixture with a genuine specimen, was obtained, and was identified by the usual tests. Distillation of the liquid portion gave a little formic acid, b. p. 100°, and a fraction, b. p. 160—170°/17 mm., which could not be identified.

Hydrolysis of the Δ^β-ester. (a) With concentrated hydrochloric acid. After hydrolysis for 2 hours, evaporation of the acid liquid on a steam-bath gave itaconic acid, m. p. and mixed m. p. 165° (Found : equiv. by microtitration, 67·7. Calc. for $C_5H_6O_4$: equiv., 65).

(b) With methyl-alcoholic potassium hydroxide. Heated for a short time on a steam-bath with a moderately concentrated solution of potassium hydroxide in dry methyl alcohol, the Δ^β-ester afforded a solid potassium salt. This was separated, washed with ether, and decomposed with cold, moderately concentrated hydrochloric acid; ether then extracted cyclopropane-1 : 1 : 2-tricarboxylic acid, m. p. [after crystallisation from ether–ligroin (b. p. 40—60°)] and mixed m. p. 187° (Found : C, 41·1; H, 3·7; equiv., by microtitration, 62·3. Calc. for $C_6H_6O_6$: C, 41·4; H, 3·45%; equiv., 58).

Addition of Hydrogen Bromide to the Unsaturated Ester.—The original unsaturated ester (65 g.) was added to 70 c.c. of 55% (wt./vol.) hydrogen bromide in acetic acid. After being kept for 3 days at room temperature, the solution was poured into ice-water and extracted with ether; the extract was washed (water, sodium carbonate solution, water), dried (calcium

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* Compounds previously assigned erroneous structures are now correctly described, and are identified by the addition, in parentheses, of the page reference (J., 1932) to their original description.

chloride), and evaporated. The residue crystallised when seeded, giving 58 g. of approximately pure methyl γ-bromo-*n*-propane-ααβ-tricarboxylate (814), m. p. 60—65°. Crystallisation from ether–ligroin raised the m. p. to 70°. With boiling methyl-alcoholic potassium iodide the γ-bromo-ester afforded the corresponding γ-iodo-ester (814), m. p. 74°. Similar addition of hydrogen bromide to the unsaturated ester, b. p. 120—140°/1 mm., recovered in the preparation of the ester (VIII) (below) gave a crystalline product, m. p. 45°, unchanged by recrystallisation from ether–ligroin. Reduction of this mixture of bromo-esters with zinc dust and boiling methyl alcohol containing 1 drop of dilute acetic acid gave methyl *n*-propane-ααβ-tricarboxylate, m. p. and mixed m. p. 48°. When a moderately dilute solution of the mixed bromo-esters, m. p. 45°, in ether–ligroin was seeded with the γ-bromo-ester, m. p. 70°, this compound alone crystallised in clusters of needles. The mother-liquor slowly deposited a small quantity of large well-formed prisms of *methyl β-bromo-*n*-propane-ααβ-tricarboxylate*, m. p. 55° after recrystallisation from ligroin (b. p. 40—60°) (Found : C, 36·3; H, 4·55; Br, 27·2. $C_9H_{13}O_6Br$ requires C, 36·4; H, 4·4; Br, 26·9%). The m. p. is depressed to 45° by admixture with the γ-bromo-ester. In one crystallisation clusters of needles, m. p. 64—65°, and prisms, m. p. 52—54°, depressed to 45° by admixture, were obtained side by side, and could be separated by hand. When an ether–ligroin solution of the γ-bromo-ester, m. p. 70°, was seeded with the β-bromo-ester, m. p. 55°, only the γ-bromo-ester, m. p. 70°, crystallised. Boiled for 24 hours with alcoholic potassium iodide, the β-bromo-ester afforded a *liquid* iodo-ester which would not crystallise even after seeding with the γ-iodo-ester, m. p. 74°.

Hydrolysis of the γ-bromo-ester with methyl-alcoholic potassium hydroxide under the same conditions as those employed with the unsaturated ester afforded *cyclo*propane-1 : 1 : 2-tricarboxylic acid (m. p. and mixed m. p.).

Conversion of Ethyl cyclo*Propane-*1 : 1 : 2-tricarboxylate into its Open-chain Isomeride.— Ethyl *cyclo*propane-1 : 1 : 2-tricarboxylate, b. p. 133—134°/1·6 mm. (Conrad and Guthzeit, *loc. cit.*), is saturated to aqueous potassium permanganate–sodium hydrogen carbonate and, after ozonolysis for 2 hours in hexane solution, evaporation of the solvent in a vacuum, decomposition with cold water and distillation, gives no precipitate with an alcoholic solution of dimedon. The same ester (1 g.) was refluxed on a steam-bath with a solution of 0·1 g. of sodium in 3 c.c. of dry methyl alcohol for 1¼ hours : the neutral fraction (unsaturated to permanganate), on similar ozonolysis, afforded formaldehyde (dimedon compound, m. p. and mixed m. p. 189—190°).

Methyl cyclo*Hexane-*1 : 1 : 2 : 4 : 4 : 5-*hexacarboxylate* (XII).—The Δ^β-propene ester (10·8 g.) was added to a cold solution of 1·15 g. of sodium in 50 c.c. of dry methyl alcohol, and the mixture refluxed on a steam-bath for 1¼ hours. The deep yellow solution was poured into brine, and the neutral fraction isolated in the usual manner. Concentration of the dry ethereal solution caused crystallisation (1·7 g.) of the *ester*, m. p. 181° after recrystallisation from absolute methyl alcohol (Found : C, 50·1; H, 5·5; *M*, in camphor, 398, 410. $C_{18}H_{24}O_{12}$ requires C, 50·0; H, 5·6%; *M*, 432). Distillation of a portion of the syrupy yellow mother-liquor (6·7 g.) afforded fractions, b. p. approx. 130°/3 mm. and 130—145°/3 mm., which were highly unsaturated and probably consisted mainly of the unchanged Δ^β-propene ester. Subsequently much decomposition set in and a small fraction of a highly viscous, yellow syrup, b. p. 220°/3 mm., was obtained. This contained unsaturated material, but, when kept with a little ether deposited crystalline material, m. p. 154—164° after recrystallisation from methyl alcohol. The m. p. was raised to 154—175° by admixture with the hexacarboxylic ester, m. p. 181°, and it is possible that the material is a further quantity of this ester possibly contaminated with a stereoisomeric form. This material was not further investigated. The neutral product isolated after the prolonged action (4 days) of 55% (wt./vol.) hydrogen bromide in acetic acid on the unsaturated residue, partly crystallised. After draining on porous porcelain and crystallisation from ether–ligroin (b. p. 40—60°), a bromine-free product, probably a *stereoisomeride*, m. p. 125—126°, was obtained (Found : C, 49·9; H, 5·6%; *M*, 351, 343). The mother-liquor slowly deposited a small amount of the γ-bromo-ester, m. p. and mixed m. p. 67—70°.

Hydrolysis of the saturated ester with boiling concentrated hydrochloric acid for 3 hours and evaporation on a steam-bath afforded crystalline *cyclo*hexane-1 : 2 : 4 : 5-*tetracarboxylic acid*, which was difficult to purify. After recrystallisation from concentrated hydrochloric acid, draining on porous porcelain, and washing with cold ether, it had m. p. 217° (decomp.) (Found : C, 42·4; H, 4·6; equiv., by microtitration, 75. $C_{10}H_{12}O_8$ requires C, 46·2; H, 4·6%; equiv., 65). It was characterised as its *methyl* ester, m. p. 88°, obtained by long esterification with methyl-alcoholic hydrogen chloride containing one drop of concentrated sulphuric acid; the neutral product crystallised and was recrystallised from ether–ligroin (b. p. 40—60°) (Found :

C, 53·1; H, 6·2. $C_{14}H_{20}O_8$ requires C, 53·2; H, 6·3%). The ester is probably a mixture of stereoisomerides. Dehydrogenation of the acid (0·2 g.), m. p. 217°, was effected by heating with powdered selenium at 310° for 2 hours. The cooled mixture was extracted with hot sodium carbonate solution, and this solution extracted with ether, acidified with hydrochloric acid, and again extracted with ether. The acid residue from the dried ethereal solution was refluxed with methyl-alcoholic hydrogen chloride for 3—4 hours. The neutral fraction gave crystalline material, m. p. 127° after one recrystallisation from ether–ligroin (b. p. 40—60°); the quantity was insufficient for further purification, but mixed with genuine methyl pyromellitate (m. p. 141°), its m. p. was raised to 138—139°.

Attempts to prepare the γ-Methoxy-ester.—The corresponding γ-bromo-ester (2·1 g.) was shaken with 1·7 g. of silver acetate in 30 c.c. of dry methyl alcohol for 12 hours. Since no apparent action had occurred, the mixture was refluxed on a steam-bath for 4 hours, cooled, and diluted with dry ether, and the silver salts removed. Evaporation of the filtrate left a colourless syrup which would not crystallise, but by distillation afforded methyl *cyclo*propane-1 : 1 : 2-tricarboxylate, b. p. 109°/0·8 mm. (Found : C, 49·7; H, 5·6; OMe, 42·6. Calc. for $C_9H_{18}O_6$: C, 50·0; H, 5·6; OMe, 43·0%). The same ester, b. p. 115°/1·0 mm., was obtained when 2 g. of the γ-bromo-ester were shaken with dry sodium methoxide (from 0·155 g. of sodium) in anhydrous ether, and the mixture left at room temperature for 18 hours. Saturated with dry ammonia in dry methyl alcohol, it afforded the *triamide*, m. p. 238° (decomp.) after crystallisation from aqueous methyl alcohol (Found : C, 43·1; H, 5·6; N, 24·6. $C_6H_9O_3N_3$ requires C, 42·1; H, 5·3; N, 24·6%).

Hydrolysis of this ester with the same solution of methyl-alcoholic potassium hydroxide as was employed in the hydrolysis of the unsaturated ester, and isolation of the acid product in the usual manner, gave a colourless syrup which immediately crystallised when rubbed. It was a *methyl dihydrogen* ester, m. p. 169°, and was purified by crystallisation from ether–ligroin (b. p. 40—60°) [Found : C, 44·8; H, 4·5; OMe, 17·9; equiv., by titration, 93·9. $C_7H_8O_6$ requires C, 44·7; H, 4·3; OMe, 16·5%; equiv. (dibasic), 94·0]. Hydrolysis with concentrated aqueous potassium hydroxide containing a little methyl alcohol gave *cyclo*propane-1 : 1 : 2-tricarboxylic acid, m. p. and mixed m. p. 187° (decomp.).

Methyl n-*Butane-ααββδδ-pentacarboxylate* (VIII) (814).—To a solution of 4·15 g. of sodium in 50 c.c. of dry methyl alcohol were added 31 g. of methyl malonate; the mixture was refluxed for 10 minutes and cooled, and a warm solution of 53·5 g. of methyl γ-bromo-*n*-propane-ααβ-tricarboxylate in dry methyl alcohol added. Separation of sodium bromide occurred with evolution of heat. The mixture was kept at room temperature for 18 hours and then refluxed on a steam-bath till neutral (2—3 hours). Distillation of the neutral fraction, isolated in the usual manner, gave a small amount of low fraction and then some recovered unsaturated ester, b. p. 120—140°/1 mm. The residue crystallised when seeded and afforded 20 g. of the butane ester, m. p. 88° * after crystallisation from ether–ligroin (b. p. 40—60°). Hydrolysis of this ester with boiling concentrated hydrochloric acid for 1 hour and complete evaporation on a steam-bath gave *n*-butanetricarboxylic acid, m. p. 120°, raised to 122° by admixture with a genuine specimen (Kay and Perkin, *loc. cit.*).

Methyl n-*Pentane-*(?)αββγγεε-*hexacarboxylate* (IX).—To a solution of 1·53 g. of sodium in 50 c.c. of dry methyl alcohol were added 23·2 g. of the butanepentacarboxylate, and the solution warmed on the steam-bath for a few minutes. To the cooled solution, 13·5 g. of methyl iodo-acetate were added; the mixture was kept at room temperature for 1¼ hours and then refluxed for 1¼ hours on a steam-bath. Distillation of the neutral fraction, isolated in the usual manner, afforded 20 g. of the *hexacarboxylate*, b. p. *ca.* 240°/4 mm., as a colourless, exceedingly viscous syrup (Found : C, 48·7; H, 5·9. $C_{17}H_{24}O_{12}$ requires C, 48·6; H, 5·7%).

The ester (20 g.) was hydrolysed for 6 hours with 60 c.c. of boiling concentrated hydrochloric acid, and the liquor evaporated to dryness on a steam-bath. The viscous residue partly crystallised, and trituration with dry ether to remove gummy material left *n*-*pentane-*(?)αβγε-*tetracarboxylic acid*, m. p. 204—205° after crystallisation from ether containing a little acetone (Found : C, 43·7; H, 5·0; equiv., by titration, 62·8. $C_9H_{12}O_8$ requires C, 43·5; H, 4·8%; equiv., 62·0). The acid is readily purified through its *barium* salt, the solubility of which is greater in cold than in hot water (Found : Ba, 46·5; H_2O, by heating an air-dried specimen at 140°, 11·1. $C_9H_8O_8Ba_2,4H_2O$ requires Ba, 46·5; H_2O, 12·2%). The last molecule of water is difficult to remove. The *methyl* ester, b. p. 180°/0·8 mm., was prepared by the action of methyl iodide on a paste of the dry silver salt and ether (Found : C, 50·9; H, 6·7. $C_{13}H_{20}O_8$ requires C, 51·3; H, 6·6%).

* The m. p. 58° previously given (*loc. cit.*) is a misprint.

Methyl cyclo*Hexanonetricarboxylate.*—The above tetramethyl ester (3 g.) in dry toluene was added to 0·23 g. of " molecular " sodium in the same medium, and the whole refluxed for 4—5 hours. The solution darkened, but much sodium remained undissolved. A drop or two of dry methyl alcohol was added and, after further refluxing to dissolve all the sodium, the cooled solution was decomposed with ice, and the alkaline solution extracted with ether. The aqueous alkaline liquor was dropped into ice-cold dilute hydrochloric acid, which was then extracted with ether. True acid products were removed by washing the extract with aqueous sodium carbonate. The quasi-acid fraction (1 g.), a yellow gum, obtained by evaporation of the dried ethereal solution, gave an intense plum colour with ferric chloride. It did not give a semicarbazone and, since the quantity was too small for successful distillation, it was extracted with dry ligroin (b. p. 40—60°). Evaporation of the ligroin solution gave a colourless, very viscous gum (ferric chloride coloration), which was analysed after removal of the last trace of solvent in a high vacuum (Found : C, 53·2; H, 6·3. $C_{13}H_{16}O_7$ requires C, 52·9; H, 5·9%).

Reduction of Methyl α-Bromo-n-propane-ααβ-tricarboxylate.—An attempt was made to convert this ester into the $\Delta^α$-propene ester by the action of silver hydroxide. No apparent action occurred when moist silver oxide, prepared from 15 g. of silver nitrate, was stirred with a solution of 17 g. of the bromo-ester in aqueous methyl alcohol at room temperature. The mixture was therefore refluxed for 6 hours, the silver bromide filtered off, and the filtrate poured into brine and extracted with ether. Distillation of the residue from the dried ethereal extract gave (together with products containing bromine) a main fraction, b. p. 132°/3 mm.—139°/2 mm., which crystallised and was identified as methyl *n*-propane-ααβ-tricarboxylate, m. p. and mixed m. p. 48°, reduction of the bromo-ester having taken place.
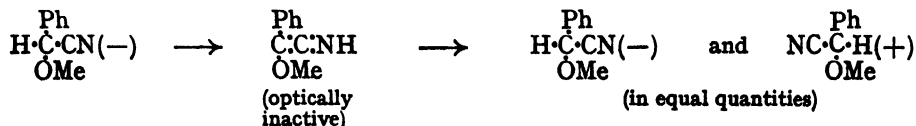
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44. (—)*Phenylmethoxyacetonitrile.*

By ISOBEL AGNES SMITH.

IN continuance of previous work on optically active nitriles (Smith, *Ber.*, 1931, **64**, 427, 1115; 1934, **67**, 1307), a study has now been made of optically active phenylmethoxyacetonitrile.

The *r*-nitrile was obtained by Hess and Dorner (*Ber.*, 1917, **50**, 390) on the lines,

$$\text{Ph·CH(OMe)·CO·NH}_2 \xrightarrow{\text{SOCl}_2} \text{Ph·CH(OMe)·CN.}$$

Several attempts were made by the author to obtain the pure optically active nitrile by this method, but the products did not give concordant values for specific rotatory power. As it was considered improbable that thionyl chloride would produce a racemising effect, its action on *r*-phenylmethoxyacetamide was investigated more fully. Two products were formed, and the separation of these by distillation was difficult. The lower-boiling fraction solidified in a freezing mixture, and was identified as benzoyl cyanide; *r*-phenylmethoxyacetonitrile was obtained as a liquid. In their description of the methoxy-nitrile Hess and Dorner made no reference to a low-boiling fraction, but in the dehydration of *r*-phenylethoxyacetamide with thionyl chloride they obtained, besides *r*-phenylethoxyacetonitrile, an unidentified low-boiling fraction with a sharp odour : doubtless this contained benzoyl cyanide.

The action of phosphoric oxide on *r*-phenylmethoxyacetamide in the presence of toluene produced the *r*-nitrile, unaccompanied by benzoyl cyanide. When this method was applied to the (+)amide, (—)*phenylmethoxyacetonitrile* was obtained in a state of optical purity as an oil, giving $[α]_D^{20°} - 53·0°$ and $[α]_{5461}^{20°} - 63·5°$ (in acetone) before and after redistillation. As was to be expected, (—)phenylmethoxyacetonitrile was very susceptible to catalytic racemisation by alcoholic potash :

$$
\begin{array}{ccccccc}
\text{Ph} & & \text{Ph} & & \text{Ph} & & \text{Ph} \\
\text{H·C·CN(—)} & \longrightarrow & \text{C:C:NH} & \longrightarrow & \text{H·C·CN(—)} & \text{and} & \text{NC·C·H(+)} \\
\text{OMe} & & \text{OMe} & & \text{OMe} & & \text{OMe} \\
& & \text{(optically} & & \text{(in equal quantities)} & & \\
& & \text{inactive)} & & & &
\end{array}
$$

A methyl-alcoholic solution containing two drops of methyl-alcoholic potash became inactive in 2 hours, but 4 hours later acquired a constant dextrorotation, $\alpha_{5461}^{20°} + 0.32°$ ($l = 2$) (see Experimental). The quantity of potash was so small that it could scarcely cause the formation of any (+)phenylmethoxyacetamide before all the (—)nitrile had been converted into r-nitrile. Now, a trace of alcoholic potash is sufficient to racemise (+)mandelonitrile and also to convert it into benzaldehyde-bis-(α-cyanobenzyl)acetal (*Ber.*, 1931, **64**, 427), and amygdalin with alcoholic potash, besides being racemised, undergoes methoxylation in the aglucone part of the molecule (*Ber.*, 1934, **67**, 1307). It is possible that an action similar to the latter had occurred to a slight extent in the present reaction; the formation of a complex of the acetal type suggested above is less probable owing to the presence of the methoxy-group.

(—)Phenylmethoxyacetonitrile in methyl-alcoholic solution underwent catalytic racemisation with water, the solution becoming optically inactive in 3 days; no small final dextrorotation was observed in this case. Under similar conditions with (+)mandelonitrile, 38 days elapsed before the solution had become inactive (*Ber.*, 1931, **64**, 427). This was in keeping with the observation of McKenzie and Smith (*J.*, 1922, **121**, 1348) that (—)phenylmethoxyacetamide was more rapidly catalytically racemised than (—)mandelamide.

The action of phenylmagnesium bromide on r-phenylmethoxyacetonitrile gave benzoin methyl ether :

$$\begin{array}{ccccc}
\text{Ph·CH·OMe} & \xrightarrow{\text{PhMgBr}} & \text{Ph·CH·OMe} & \xrightarrow{\text{H}_2\text{O}} & \text{Ph·CH·OMe} & \xrightarrow{\text{HCl}} & \text{Ph·CH·OMe} \\
\text{CN} & & \text{Ph·C:NMgBr} & & \text{Ph·C:NH} & & \text{COPh}
\end{array}$$
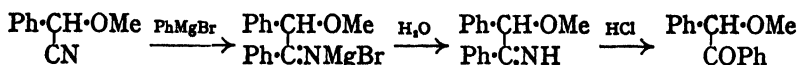
(cf. *Ber.*, 1931, **64**, 427; McKenzie and Kelman, *J.*, 1934, 412). (—)Benzoin methyl ether was obtained by McKenzie, Martin, and Rule (*J.*, 1914, **105**, 1583) from (—)phenylmethoxyacetamide and phenylmagnesium bromide.

The interaction of phenylmagnesium bromide and benzoyl cyanide gave triphenylcarbinol :

$$\text{Ph·CO·CN} \xrightarrow{\text{PhMgBr}} \text{Ph·COPh} \xrightarrow{\text{PhMgBr}} \text{Ph}_3\text{C·OMgBr} \longrightarrow \text{Ph}_3\text{C·OH}$$

This displacement of the cyano- by an aryl group in the Grignard reaction recalls the formation of triphenylcarbinol by the action of phenylmagnesium bromide on oxamethane or ethyl cyanoformate (McKenzie and Duff, *Ber.*, 1927, **60**, 1335).

EXPERIMENTAL.

The Interaction of Thionyl Chloride and (—)*Phenylmethoxyacetamide.*—6·5 G. of (—)phenylmethoxyacetamide ($[\alpha]_D^{19°} - 103·6°$ in acetone; $c = 3·1465$) were heated with 20 g. of specially purified thionyl chloride (Meyer, *Monatsh.*, 1913, **34**, 569) for 44 hours at 70—80°. The excess of thionyl chloride was removed under diminished pressure, the residual oil poured into water and extracted with ether, and the resulting oil distilled twice. The fraction, b. p. 95°/0·4 mm., gave with concentrated sulphuric acid the characteristic magenta coloration of the nitrile. In acetone ($l = 2$, $c = 1·842$): $\alpha_{5461}^{20°} + 1·65°$, $[\alpha]_{5461}^{20°} + 44·8°$. From another experiment with the (+)amide the product gave a higher value, *viz.*, $[\alpha]_{5461}^{20°} - 57·2°$ ($l = 2$, $c = 5·2505$).

The Interaction of Thionyl Chloride and r-*Phenylmethoxyacetamide.*—21·5 G. of r-phenylmethoxyacetamide (m. p. 111—112°) were heated for 48 hours at about 90° with 50 c.c. of purified thionyl chloride. The procedure was as above, but the extraction was carried out with benzene, since any unchanged amide would be less soluble in this solvent. The residual oil was distilled at 20 mm., three fractions being collected : (I) b. p. 102—110°, (II) b. p. 110—117°, (III) b. p. 117—118°. Fraction (I) contained some of the nitrile, since it gave the characteristic magenta coloration with concentrated sulphuric acid, but when cooled in a freezing mixture it deposited benzoyl cyanide, m. p. (after two recrystallisations from light petroleum) and mixed m. p. (with an authentic specimen) 31—32° (Found : C, 73·2; H, 3·8; N, 10·3. Calc. for C_8H_5ON : C, 73·3; H, 3·8; N, 10·7%).

Benzoyl cyanide was a product of an experiment in which the thionyl chloride (Kahlbaum) used was not specially purified, and also of another carried out at 70°.

Dehydration of r-*Phenylmethoxyacetamide with Phosphoric Oxide in Presence of Toluene.*—An intimate mixture of the amide (15·4 g.) and the oxide (21 g.) was heated in dry toluene at 110°

for 4 hours. The toluene was decanted, the residue washed with hot toluene, the solvent removed under diminished pressure, and the residual oil distilled; b. p. 120°/17 mm. Yield, 7·3 g. of *r*-nitrile.

Dehydration of (+)*Phenylmethoxyacetamide with Phosphoric Oxide in Presence of Toluene.*— 12 G. of (+)phenylmethoxyacetamide, prepared from (+)phenylmethoxyacetic acid (Pirie and Smith, J., 1932, 338) and having m. p. 108—109° and $[\alpha]_D$ + 104·1° in acetone, were treated with 16·5 g. of phosphoric oxide in presence of toluene as described above. (−)*Phenylmethoxyacetonitrile* was obtained as a colourless oil (5·1 g.), b. p. 120°/17 mm. (Found : C, 73·0; H, 6·3; N, 9·7. C_9H_9ON requires C, 73·4; H, 6·1; N, 9·5%). In acetone ($l = 2$, $c = 4·936$) : $\alpha_D^{20°}$ − 5·23°, $[\alpha]_D^{20°}$ − 53·0°; $\alpha_{5461}^{20°}$ − 6·27°, $[\alpha]_{5461}^{20°}$ − 63·5°.

Catalytic Racemisation of (−)*Phenylmethoxyacetonitrile with Methyl-alcoholic Potash.*—The (−)nitrile (0·9843 g.) was made up to 20 c.c. with dry methyl alcohol ($l = 2$, $c = 4·9215$) : $\alpha_D^{20°}$ − 5·31°, $[\alpha]_D^{20°}$ − 53·9°; $\alpha_{5461}^{20°}$ − 6·31°, $[\alpha]_{5461}^{20°}$ − 64·1°. Two drops of methyl-alcoholic potash (1·043N) were added to about 16 c.c. of the solution :

t, mins.	2	5	10	20	30	40	50	60	70
$\alpha_{5461}^{20°}$	−5·97°	−5·55°	−4·80°	−3·63°	−2·77°	−1·99°	−1·51°	−1·04°	−0·75°

t, mins.	80	90	99	110	119	4 hrs.	24 hrs.	4 days
$\alpha_{5461}^{20°}$	−0·49°	−0·27°	−0·15°	−0·06°	0·00°	+0·33°	+0·32°	+0·32°

The final dextrorotation was unexpected, and in case this was due to a trace of (+)phenyl-methoxyacetamide present in the (−)nitrile the preparation of the latter was repeated, with the further precaution of carrying out the distillation of the nitrile under diminished pressure in presence of a small amount of phosphoric oxide. The (−)nitrile so obtained gave in methyl alcohol ($l = 2$, $c = 5·0535$) : $\alpha_{5461}^{20°}$ − 6·49°, $[\alpha]_{5461}^{20°}$ − 64·2°. Two drops of methyl-alcoholic potash (1·043N) were added to about 18 c.c. of this solution; after 24 hours, $\alpha_{5461}^{20°}$ + 0·28° was observed.

Catalytic Racemisation of (−)*Phenylmethoxyacetonitrile with Water.*—The (−)nitrile (0·7206 g.) was made up to 20 c.c. with dry methyl alcohol ($l = 2$, $c = 3·603$) : $\alpha_{5461}^{20°}$ − 4·56°, $[\alpha]_{5461}^{20°}$ − 63·3°. 1 C.c. of water was added to this solution :

t	2 mins.	110 mins.	4·5 hrs.	28·5 hrs.	33 hrs.	46 hrs.	54 hrs.	3 days	6 days
α	−4·37°	−4·16°	−3·77°	−1·50°	−1·28°	−0·34°	−0·17°	+0·03°	+0·03°

Action of Phenylmagnesium Bromide on r-*Phenylmethoxyacetonitrile.*—An ethereal solution of *r*-phenylmethoxyacetonitrile (7·2 g.), prepared by dehydration of the *r*-amide with phosphoric oxide, was added within 3 minutes to the Grignard reagent, prepared from bromobenzene (23·2 g.). The mixture was heated for 15 minutes. After 1 hour at the ordinary temperature, the complex was decomposed with ice and concentrated hydrochloric acid and the ethereal layer was separated immediately. From the acid layer, *r*-benzoin methyl ether (1·4 g.), m. p. 48—49°, was obtained.

Action of Phenylmagnesium Bromide on Benzoyl Cyanide.—The Grignard reagent, prepared from bromobenzene (24 g.), was added at intervals to an ethereal solution of benzoyl cyanide (3·7 g., m. p. 32°). The mixture was heated for ¼ hour and then decomposed with ice and concentrated hydrochloric acid, and the ethereal layer was separated immediately. From the latter were obtained 2·8 g. of triphenylcarbinol, m. p. and mixed m. p. 161—162°.

45. *A Rearrangement of* o-*Aminodiphenyl Ethers. Part II.*

By KENNETH C. ROBERTS, CHARLES G. M. DE WORMS, and (MISS) HILDA B. CLARK.

IN extension of the observations recorded in Part I (Roberts and de Worms, J., 1934, 727) an investigation has now been made of the influence of a number of nuclear sub-stituents in the 4-position [I; R = NH_2, OMe, Me, H, I, Br, Cl, $CO·O·C_6H_3(NO_2)_2$, CO_2H] on the behaviour of *o*-aminodiphenyl ethers of type (I, X = H).

The seven ethers in the sequence from the 4-amino-derivative to the 4-chloro-derivative all undergo rearrangement to the isomeric 5-substituted *o*-hydroxydiphenylamines of
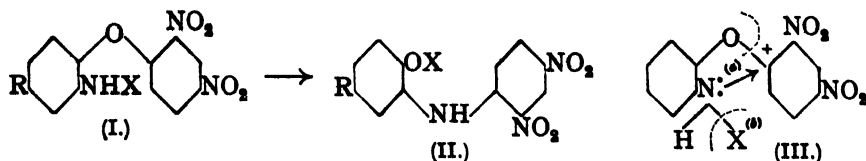
type (II, X = H). The condition most favourable to the rearrangement was in all cases the same as that recorded in the earlier work, *viz.*, the presence of very slightly ionisable basic or hydroxylic solvents such as alcohol and pyridine, particularly in presence of water. The 4-carboxy-ether and its dinitrophenyl ester, however, proved stable under all the conditions investigated.

It is suggested that two factors determine the proneness of the ethers to rearrange: (*a*) the ability of an unshared electron pair of the *o*-amino-nitrogen to form a co-ordinate link with the positive α-carbon atom of the second nucleus (cf. III and also Kent and Smiles, J., 1934, 422); and (*b*) the ability of a group X attached to the *o*-amino-nitrogen to become a free positively charged radical, in the present examples, proton. In presence of these factors the molecules of a hydroxylic or weakly basic solvent may operate to effect the change (I ⟶ II). When the rearrangement is brought about by the action of heat alone, it appears that the substance itself may be regarded as a basic solvent for the rearranging molecules. The inductive effect of a particular substituent R could clearly facilitate the operation of one of these factors only while retarding the operation of the other, and it therefore appears that an optimum condition for the change might occur when R is a group having an intermediate value of the inductive effect. The rates of rearrangement of the active ethers have been compared by a comparative method depending on the marked difference in colour between equimolecular solutions of a given ether

R	OH	OBz	NH₂	OMe	Me	H	I	Br	Cl	CO₂Ar CO₂H	NO₂
Time (mins.) for complete change	Ethers not obtd.		50	13	7	5	15	30	60	No change	Ether not obtd.

Increasing — *I* ← → Decreasing — *I*   +*I*

and of its isomeric diphenylamine. The results (see table) show a distinct maximum for the rate of change when R = H. On the above view the retardation in the direction of increasing — *I* will be due to inhibition of the operation of factor (*b*), while that in the direction of decreasing — *I* will be due to the reduced availability of the lone electrons of nitrogen (factor *a*). The extreme cases of complete inhibition of the rearrangement are met with when R (= CO₂Ar and CO₂H) has a positive inductive effect. It has not been possible to extend the series in the direction either of increasing — *I* or of increasing + *I*, owing to difficulties attending the synthesis of the 4-hydroxy- and the 4-nitro-ethers (I, R = OH and NO₂). It is hoped to throw further light on the mechanism of the rearrangement by a study both of a variety of *N*-substituted derivatives (I and II, X = acyl and alphyl) and also of a series of 5-substituted *o*-aminodiphenyl ethers.

The new diphenyl ethers described have been obtained by condensing 1-chloro-2 : 4-dinitrobenzene with the sodium or potassium derivative of the appropriate *o*-aminophenol (IV) under very mild conditions. Condensation of the disodio-derivative of 3-amino-*p*-hydroxybenzoic acid was, however, carried out with two mols. of chlorodinitrobenzene to yield the dinitrophenyl ester (V), which was hydrolysed to the free acid.
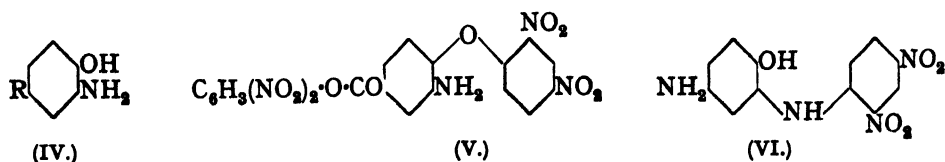
In general, condensation of the phenol (IV) with chlorodinitrobenzene in presence of sodium acetate under usual conditions gave the corresponding dinitrodiphenylamine, but 2′ : 4′-*dinitro-5-amino-2-hydroxydiphenylamine* (VI) could not be obtained by use either of 2 : 4-diaminophenol, which gives the isomeric 3-amino-4-hydroxydiphenylamine (D.R.-P. 107,971), or of its 4-acetyl derivative, which proved too liable to oxidation for the purpose. But when sodium 2 : 4-diacetamidophenoxide was condensed with excess of chlorodinitrobenzene, hydrolysis of the 2-acetamido-group occurred and was accompanied by rearrangement of the resulting ether, with formation of 2′ : 4′-*dinitro-5-acetodinitro-phenylamido-2-hydroxydiphenylamine*, which on hydrolysis yielded the required substance (VI). The *o*-aminophenols (IV) were in general prepared by hydrosulphite reduction of the corresponding nitro-compound, but 2 : 4-diaminophenol was obtained by acid reduction (iron) of 2 : 4-dinitrophenol (D.R.-P. 269,542). 2-Nitro-*p*-iodophenol was most conveniently obtained by direct nitration of *p*-iodophenol.

EXPERIMENTAL.

Comparison of the Rates of Rearrangement of Diphenyl Ethers.—The figures recorded in the table (above) were arrived at by adding 0·0005 g.-mol. of the ether to 12·5 c.c. of an acetic acid–pyridine mixture (4 : 1) at 50° and observing the time occupied by this solution in reaching the same tint as that of an identical solution of the isomeric diphenylamine, also at 50°.

2-*Aminoquinol* 4-*Benzoate* (IV, R = OBz).—2-Nitroquinol 4-benzoate (*Ber.*, 1893, **26**, 1909; 1916, **49**, 1401), dissolved in aqueous alcohol, was treated at the boiling point with sodium hydrosulphite (*q.s.*). The cooled filtered solution on addition of much water yielded 2-*aminoquinol* 4-*benzoate* as colourless needles; recrystallised from aqueous alcohol, this formed colourless plates, m. p. 161—164° (darkening) (Found : C, 67·9; H, 4·6. $C_{13}H_{11}O_3N$ requires C, 68·1; H, 4·8%).

2′ : 4′-*Dinitro*-2 : 4-*diaminodiphenyl Ether* (I; R = NH$_2$, X = H).—2 : 4-Diaminophenol dihydrochloride (1 mol.), from 2 : 4-dinitrophenol (D.R.-P. 269,542), in contact with alcohol was treated with an alcoholic solution of 1-chloro-2 : 4-dinitrobenzene (1 mol.), and to the mixture was added at room temperature sodium ethoxide (3 mols.) in alcohol. The reacting mixture was cooled in running water and then kept for 1 hour. The crystalline product, recrystallised from alcohol (charcoal), gave the *ether* as a dark orange substance, soluble in hydrochloric acid, insoluble in aqueous caustic soda. It sintered at 166—170°, then darkened, and finally decomposed at 181° (Found : C, 49·5; H, 4·8. $C_{12}H_{10}O_5N_4$ requires C, 49·6; H, 3·4%).

2′ : 4′-*Dinitro*-5-*amino*-2-*hydroxydiphenylamine* (VI).—(a) When a solution of the isomeric ether (above) in aqueous pyridine was warmed, it rapidly darkened, and on treatment with water yielded a brown flocculent material, which formed a sparingly soluble, black sodium derivative with aqueous caustic soda. Crystallised from alcohol (charcoal), the *diphenylamine* formed small red plates, which turned dark purple at 225—230° and decomposed at 237—240° (Found : C, 49·2; H, 3·8%). The diphenylamine was also obtained by rearrangement of the ether either in aqueous-alcoholic solution or on heating it alone at about 150°.

(b) 2 : 4-Diacetamidophenol (*Bull. Soc. chim.*, 1905, **33**, 785) (1 mol.) in alcohol was treated with sodium ethoxide (1 mol.), and the mixture with chlorodinitrobenzene (1 mol.). The liquid rapidly darkened and deposited sodium chloride but no organic matter. After 1 hour the liquid, freed from sodium chloride, was treated with much water; a deep red, flocculent solid, insoluble in hydrochloric acid and forming a sparingly soluble sodium derivative with aqueous caustic soda, then resulted. It separated from alcohol in dark red crystals of 2′ : 4′-*dinitro*-5-*acetodinitrophenylamido*-2-*hydroxydiphenylamine*, which turned yellow at 135° and decomposed above 250° (Found : C, 47·8; N, 16·9. $C_{20}H_{14}O_{10}N_6$ requires C, 48·1; N, 16·8%). Treatment of this substance at 100° for 1½ hours with concentrated hydrochloric acid yielded a red solution, which on treatment with water and sodium bicarbonate deposited a reddish flocculent solid; this after purification from alcohol was identical with the product described under (a) (Found : N, 19·3. $C_{12}H_{10}O_5N_4$ requires N, 19·3%).

2′ : 4′-*Dinitro*-2-*amino*-4-*methoxydiphenyl Ether* (I; R = OMe, X = H).—2-Nitro-4-methoxyphenol (Robinson and Smith, J., 1926, 392) in aqueous alcohol was treated on the water-bath with sodium hydrosulphite (*q.s.*). The product was filtered hot, the filtrate depositing white plates, m. p. 124°, in 70% yield. The aminomethoxyphenol, being unstable, was analysed as the *hydrochloride*, white needles, m. p. 171° (Found : Cl, 20·5. $C_7H_9O_2N,HCl$ requires Cl, 20·2%).

The above hydrochloride (1 mol.), treated for 2—3 hours at room temperature with alcoholic potassium ethoxide (2 mols.) and chlorodinitrobenzene (1 mol.), deposited crystals of 2′ : 4′-*dinitro-2-amino-4-methoxydiphenyl ether*, which, washed with water and recrystallised from benzene, formed yellow needles, m. p. 178° (yield, 40%) (Found : C, 51·1; H, 3·5. $C_{13}H_{11}O_6N_3$ requires C, 51·1; H, 3·6%). An unidentified substance, m. p. 78°, was isolated from the alcoholic filtrate, but none of the isomeric diphenylamine was observed.

2′ : 4′-*Dinitro-2-hydroxy-5-methoxydiphenylamine* (II; R = OMe, X = H).—(a) A pyridine solution of the above diphenyl ether slowly darkened at room temperature, and the isomeric diphenylamine was isolated. The rearrangement took place very rapidly in hot aqueous pyridine, hot aqueous alcohol, or hot aqueous acetic acid, slowly in absolute alcohol or hot aqueous caustic soda, but not at all in glacial acetic acid, benzene, or acetone.

(b) 2-Amino-4-methoxyphenol hydrochloride (1 mol.) in alcohol was treated with chlorodinitrobenzene (1 mol.) in presence of anhydrous sodium acetate under usual conditions. Treatment of the resulting solution with water yielded a red flocculent solid, which crystallised from acetic acid in needles, m. p. 157° (Found : C, 51·2; H, 3·4. $C_{13}H_{11}O_6N_3$ requires C, 51·1; H, 3·6%). The *diphenylamine* was chromoisomeric, becoming violet-black at 100°.

2′ : 4′-*Dinitro-2-aminodiphenyl Ether.*—o-Aminophenol (5·5 g.) in absolute alcohol (50 c.c.) containing sodium ethoxide (1 mol.) was treated below 20° with chlorodinitrobenzene (1 mol.). The shaken mixture after some minutes deposited the crystalline *ether*, which was collected after 3 hours, washed (yield, 45%), and recrystallised from benzene, forming bright yellow plates, m. p. 123° (Found : C, 52·2; N, 15·5. $C_{12}H_9O_5N_3$ requires C, 52·3; N, 15·2%). From the red alcoholic filtrate, the isomeric 2′ : 4′-dinitro-2-hydroxydiphenylamine was isolated. This was also prepared by usual methods, and from the above ether in contact with water or aqueous alkali or in warm pure or aqueous alcohols or pyridine; acetic acid, except in hot aqueous solution, acted only very slowly.

2′ : 4′-*Dinitro-4-aminodiphenyl Ether.*—p-Aminophenol (5·5 g.) in alcohol (100 c.c.) containing sodium ethoxide (1 mol.) was poured slowly into alcohol (50 c.c.) containing chlorodinitrobenzene (1 mol.), the temperature being kept below 20°. After 3 hours the *ether* was collected and crystallised from benzene, forming small orange prisms, m. p. 223° (decomp.) (Found : N, 15·4. $C_{12}H_9O_5N_3$ requires N, 15·2%). This ether gave no indication of rearrangement in the usual solvents.

4-*Iodo-2′ : 4′-dinitro-2-aminodiphenyl Ether.*—Difficulty being encountered in the preparation of 4-iodo-2-nitrophenol by Hodgson's method (J., 1927, 1141), p-iodophenol (11 g.) in glacial acetic acid (80 c.c.) was added slowly to glacial acetic acid (50 c.c.) containing fuming nitric acid (6·3 g.). The product, poured on ice, gave the iodonitrophenol in 75% yield. This was purified by distillation in steam, and reduced in alkaline solution with sodium hydrosulphite.

4-Iodo-2-aminophenol (2·3 g. in well-cooled alcohol, 20 c.c., containing potassium ethoxide, 1 mol.) was poured slowly into alcohol (20 c.c.) containing chlorodinitrobenzene (2 g.) below 20°. After 3 hours, the crystals were washed with alcohol and with water and recrystallised from benzene or acetic acid, bright yellow needles, m. p. 125°, of 4-*iodo-2′ : 4′-dinitro-2-amino-diphenyl ether* being obtained (Found : C, 36·1; N, 10·4. $C_{12}H_8O_5N_3I$ requires C, 35·9; N, 10·4%).

5-*Iodo-2′ : 4′-dinitro-2-hydroxydiphenylamine.*—(a) Treatment of the above ether with hot aqueous alkali or water effected the usual rearrangement to the isomeric diphenylamine, which proceeded more rapidly in alcohol or pyridine. Glacial acetic acid was without effect on the ether.

(b) Equimolecular quantities of 4-iodo-2-aminophenol (5 g.), chlorodinitrobenzene, and anhydrous sodium acetate in alcohol (100 c.c.) were heated on the water-bath (2 hours). The product, isolated by usual methods, crystallised from alcohol in long red-brown needles or from glacial acetic acid in small prisms, m. p. 145° (Found : C, 35·6; H, 2·6. $C_{12}H_8O_5N_3I$ requires C, 35·9; H, 2·0%).

4-*Bromo-2′ : 4′-dinitro-2-hydroxydiphenyl Ether.*—4-Bromo-2-nitrophenol (5 g.) in aqueous caustic soda (large excess) was treated at 80° with sodium hydrosulphite (q.s.). Acidification of the resulting colourless solution with acetic acid gave the corresponding aminophenol in 90% yield.

The usual reaction (4-bromo-2-aminophenol, 4·5 g., alcohol, 40 c.c., sodium ethoxide, 1 mol.; alcohol, 20 c.c., chlorodinitrobenzene, 5 g.; below 20°) gave the *ether* (55% yield), which, recrystallised from benzene or glacial acetic acid, formed yellow plates, m. p. 140° (Found : C, 40·7; N, 12·0. $C_{12}H_8O_5N_3Br$ requires C, 40·6; N, 11·8%).

5-*Bromo-2′ : 4′-dinitro-2-hydroxydiphenylamine.*—(a) The usual rearrangement of the cor-

responding ether was effected by pyridine or alcohol, pure or aqueous; also by aqueous alkali or water, but very slowly.

(b) Condensation of 4-bromo-2-aminophenol, chlorodinitrobenzene, and sodium acetate by the usual method gave the *diphenylamine* in 75% yield. It crystallised from alcohol in deep red needles and from glacial acetic acid in crimson plates, m. p. 190° (Found : C, 40·7; N, 12·2. $C_{12}H_8O_5N_3Br$ requires C, 40·6; N, 11·8%), readily soluble in aqueous alkali.

4-Chloro-2′ : 4′-dinitro-2-aminodiphenyl ether, obtained in 60% yield (4-chloro-2-aminophenol, 3·7 g., alcohol, 100 c.c., sodium ethoxide, 1 mol.; alcohol, 40 c.c., chlorodinitrobenzene, 5 g.), formed yellow needles from benzene or glacial acetic acid, m. p. 152° (Found : C, 46·3; N, 13·6. $C_{12}H_8O_5N_3Cl$ requires C, 46·5; N, 13·5%).

5-Chloro-2′ : 4′-dinitro-2-hydroxydiphenylamine.—(a) Rearrangement of the ether took place slowly in pyridine, alcohol, aqueous acetic acid, and water.

(b) Condensation of 4-chloro-2-aminophenol and chlorodinitrobenzene gave the *diphenylamine* (long, deep red needles from alcohol, crimson plates from acetic acid; m. p. 215°) in 80% yield (Found : C, 46·3; N, 13·6. $C_{12}H_8O_5N_3Cl$ requires C, 46·5; N, 13·5%).

2′ : 4′-Dinitro-2-amino-4-carboxydiphenyl Ether.—3-Nitro-4-hydroxybenzoic acid was obtained in 75% yield by treating *p*-hydroxybenzoic acid (0·1 mol.) in glacial acetic acid (100 c.c.) with fuming nitric acid (0·1 mol.) in glacial acetic acid (20 c.c.) at 30—40°, the mixture being poured on ice after 15 minutes.

3-Amino-4-hydroxybenzoic acid resulted in 70% yield when an alkaline solution of the nitro-acid on the steam-bath was treated with sodium hydrosulphite (*q.s.*), cooled, and carefully acidified with acetic acid.

When a solution of 3-amino-4-hydroxybenzoic acid (1 mol.) in alcohol containing potassium ethoxide (2 mols.) was treated at room temperature for 30 minutes with chlorodinitrobenzene (2 mols.) in alcohol, the 2 : 4-*dinitrophenyl* ester (V) of 2′ : 4′-dinitro-2-amino-4-carboxydiphenyl ether separated in excellent yield; it crystallised from alcohol in white spear-like needles, m. p. 89° (Found : C, 46·8; H, 2·8. $C_{19}H_{11}O_{11}N_5$ requires C, 47·0; H, 2·2%). The substance was not affected by prolonged contact with aqueous pyridine, even at 170° in a sealed tube. On treatment of the ester with hot aqueous caustic soda, yellow needles separated which appeared to be the sodium salt of the corresponding *carboxylic acid*. Treatment of the alkaline mixture with concentrated hydrochloric acid yielded a pale cream solid, which was purified from alcohol as cream-coloured needles, m. p. 115° (Found : C, 48·7; H, 2·9. $C_{13}H_9O_7N_3$ requires C, 48·9; H, 2·8%). Aqueous pyridine, alcohol, acetic acid and alkali were all without action on the substance.

The 2 : 4-*dinitrophenyl* ester of 2′ : 4′-dinitro-2-hydroxy-5-carboxydiphenylamine [II; R = CO·O·$C_6H_3(NO_2)_2$, X = H] resulted when 3-amino-4-hydroxybenzoic acid (1 mol.) in alcohol was treated with chlorodinitrobenzene (2 mols.) in presence of anhydrous sodium acetate under reflux for 2—3 hours. The product which resulted when the mixture was poured into water was taken up in aqueous alkali, and the dinitrophenyl ester was isolated from the filtered alkaline solution by addition of hydrochloric acid (60% yield). It formed reddish-orange needles from glacial acetic acid, m. p. 155° (Found : C, 46·9; H, 2·5. $C_{19}H_{11}O_{11}N_5$ requires C, 47·0; H, 2·2%). Hot aqueous alkali (30 mins.) converted the ester into the corresponding *carboxylic acid*, which was isolated from the red alkaline solution as a yellow solid and was obtained as deep yellow, microcrystalline needles, m. p. 185°, by precipitation with acid from its solution in alcoholic ammonia (Found : C, 48·7; H, 3·2. $C_{13}H_9O_7N_3$ requires C, 48·9; H, 2·8%). The substance was stable towards aqueous pyridine.

4 : 2′ : 4′-*Trinitro-2-aminodiphenylamine* (II; R = NO_2, X = H) resulted when equimolecular quantities of 4-nitro-2-aminophenol (Amer. Pat. 1,689,014), anhydrous sodium acetate, and chlorodinitrobenzene in alcohol were heated under reflux. It was purified from alcohol as a bright yellow substance, m. p. 225° (decomp.), which formed a dark-coloured sodium derivative with aqueous caustic soda (Found : C, 45·2; H, 3·4. $C_{12}H_8O_7N_4$ requires C, 45·0; H, 2·5%). Treatment of the nitroaminophenol with chlorodinitrobenzene in alcohol in presence of sodium ethoxide or potassium ethoxide yielded the same substance. Under no conditions tried was the isomeric trinitroaminodiphenyl ether obtained.

Unicellular Chemistry. The Part Played by External Influences in Determining the Chemical Character and Biological Behaviour of Unicellular Organisms.

DELIVERED BEFORE THE CHEMICAL SOCIETY ON MAY 3RD, 1934.

By J. VARGAS EYRE, Ph.D., F.I.C.

WHEN opening a discussion on " Unicellular Chemistry " on May 3rd, 1934, I expressed the view that too frequently insufficient regard is paid to facts concerning the cell itself in speculations as to the course of biochemical change which it brings about when in contact with various media. The theme of the cell itself, rather than what it can do, was chosen with a view to stressing the important part which questions of nutrition, conditions of growth, condition of cell membrane, and mutation play in determining the subsequent activity of unicellular organisms. These factors are frequently over-looked by those studying extra-cellular biological changes brought about by such organisms; consequently, no little confusion arises, particularly on questions of vitamin potency and of enzymic activity, and much recorded work is valueless. It was felt that the gist of observation, extending over a number of years, bearing upon these and other questions concerning the cell itself would be of interest to other workers in the same field.

Unusual opportunities are afforded by the research organisation of the Distillers Company Limited for studying questions of this kind in connexion with yeast manufacture on a large scale. For example, one is able to study the influence of the medium in which the cell grows, the influence of temperature, of aeration, and of many other factors upon the chemical and biological character of the cells themselves over some fifty million multiplications and through many generations on a large scale under rigidly controlled conditions. In this way it is possible to study factors which in large measure seem to determine the chemical and biological behaviour of the final cell.

It is well known that certain moulds, when grown from the same pure culture but on different media, show marked differences in their outward appearance and in their manner of growth. It may be urged that moulds are not unicellular organisms; but some are, for example, the *Mucors*, although others grow in chains and clusters, but the same applies to yeasts and to bacteria, which, under some conditions, also grow in chains and clusters. It is largely a matter of nutrition and of conditions of growth, as indeed seems to be the case where other cell differences are concerned, which, although not so easy to demonstrate and appreciate, are no less profound. The late Professor R. Chodat, when cultivating *Phoma* on different media, found that variation of the proportion of carbohydrate in the medium exercises an effect on the growth, the colour, and the morphology of the organisms. Increased sugar promotes more active growth and intensity of colour, whilst diminished quantities of sugar reduce mycelial growth. Further, variation of the nitrogen content of the same medium also markedly influences the growth, the colour, and the morphology; the growth being decreased by increased nitrogen, the colour intensity increased and the conidial growth restricted by shortage of nitrogen. The colour differences and the growth differences in these cases are not caused by a change of p_{H} due to growth products, nor to the selective use in part only of the nutrient salts contained in the medium on which growth takes place, although there are, of course, instances of this kind, and also cases where the type of growth and power of developing colour and other obvious signs of difference are brought about by changes of temperature, through the influence of light, and through other cultural conditions. The following photographs of preparations of *Isaria* by C. E. Grover afford interesting examples of this kind. Fig. 1 shows growth with carbohydrate deficiency; Fig. 2, growth in the dark with carbohydrate in plenty; and Fig. 3, growth with carbohydrate in plenty when exposed to the light on one side only, providing a good example of heliotropism.

Great importance is attached to evidence brought forward by H. B. Hutchinson and T. B. Bright as a result of observations over a number of years, that differences, although

less obvious than in the above examples of *Phoma* and of *Isaria*, are frequently shown by individual strains of yeast derived from a single original mother-cell. Although the medium on which these strains are grown is identical in all cases, the resulting growths—giant colonies—from single cells exhibit marked variations in size, colour, general configuration, and enzymic activity, reflecting to some extent the character of the individual cells of which the growths are composed. In the absence of any evidence of actual conjugation of the cells, one has to admit some sudden and unexpected jump, something equivalent to the idea of mutation, carrying with it changes in appearance and properties of the resulting cell; an interesting feature being that these variations from the original cell are in some cases heritable.

An illustration of this kind, due to genetic rather than to physiological factors, is furnished by the following series of photographs (Fig. 4) of giant colonies of yeast from the work of H. B. Hutchinson and T. B. Bright. In this series each giant colony was derived from a single cell taken from one and the same culture and grown on the same medium. That shown as A is regarded as similar in all respects to the original culture from which the series was derived and may be taken as representing the parent stock; B and C are obviously different, whilst the colony shown as D, although apparently similar in appearance to A, is composed of cells the enzymic activity of which is markedly greater than that of the original mother-cell from which the colony was derived.

Equally striking examples are also obtained when similar giant colonies, all derived from the same culture from the same cell, are grown on media of different compositions. In these cases, too, the enzymic and other properties of the variants are found to have changed in degree of intensity of activity. A further example of this is given in Fig. 5, which represents two colonies derived from the same culture, but grown (A) on a normal gelatin medium and (B) on the same medium to which have been added the products of the growth of (A). Marked difference is found between yeast colonies grown in these circumstances.

In unicellular organisms metabolic changes are governed primarily by the activity of the enzymes contained within the cell and by the condition or permeability of the cell wall, which regulates and promotes relatively enormous transfers of material. One knows that within a certain range of acidity or alkalinity the cell wall may change markedly and as a consequence osmosis may proceed quite differently; for example, the free entry of nutrient materials may be hindered or facilitated either generally or selectively, or enzymes of the cell may become more active or less active as a consequence of change in the penetrability of the membrane.

Far too little regard is paid to the important part played by the surface condition of micro-organisms as determining chemical change. One has grown accustomed to the rapid and remarkable chemical changes brought about at the surface of inorganic catalysts and one has learned to appreciate the necessity of having these active surfaces of the right kind and under rigidly controlled conditions. With micro-organisms the ratio of surface to substance is extremely high and for the most part enzymic changes take place at the surface of the organisms. Yet these questions of membrane condition are often overlooked in considerations of the mechanism of enzyme reactions. Again, a change of condition of the membrane may be sufficient to cause an agglutination of otherwise single free-moving cells so that they form mass groupings, thus giving an entirely different outward appearance, apart from colour. Further, the membrane may be the seat of base exchange, as indeed seems to be the case with starch grains.

The enzymic activity of the cell content shows an interesting gradation from quite simple to highly complex functions; for example, in the case of the action of yeast on sugars, one has the following series showing increasing enzymic versatility :

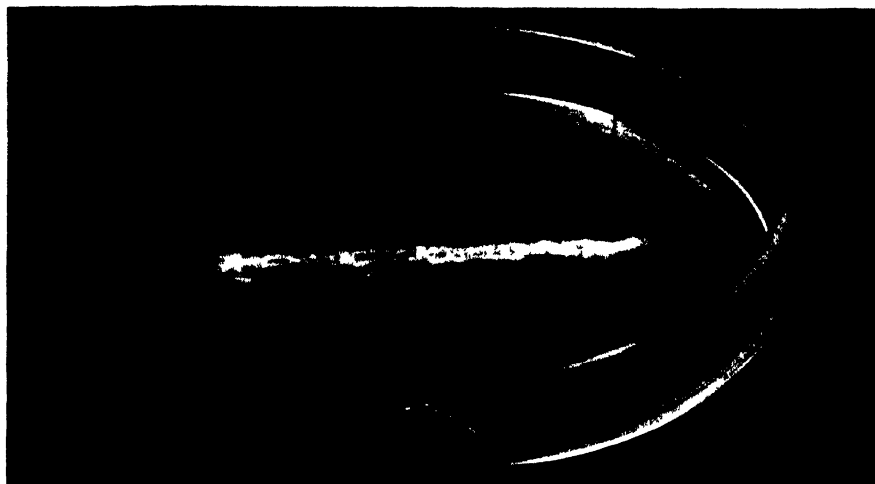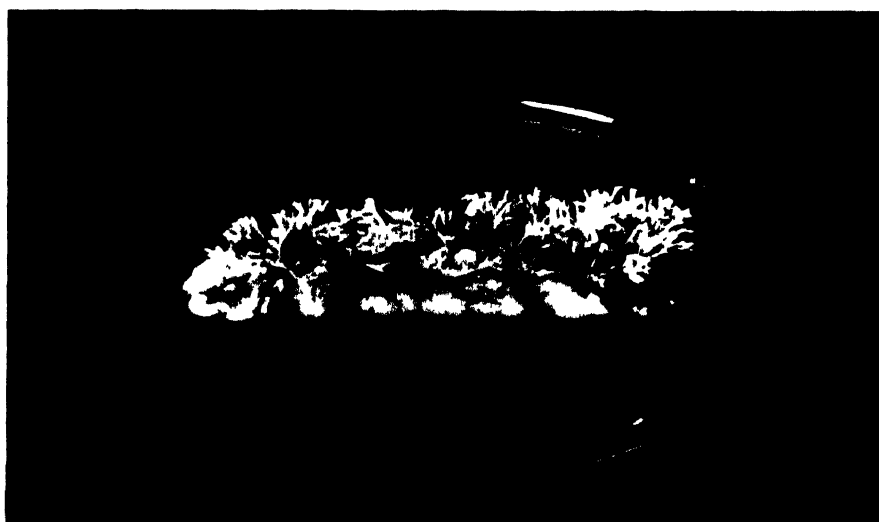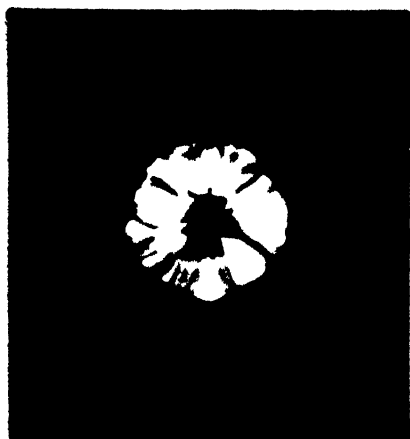| Enzymes.	Organism.	Acts upon
No saccharide splitting. Growth only	*Hansenula belgica*	No fermentation of hexoses
No saccharide splitting, merely fermenting	*Sacc. apiculatus*	Only the simple, closely related hexoses (glucose, fructose, and mannose)
Invertase	*Torula dattila*	Saccharose, glucose, fructose, mannose

Fig. 1.

Fig. 2.

Fig. 3

Isaria

A   B

FIG. 4

C   D
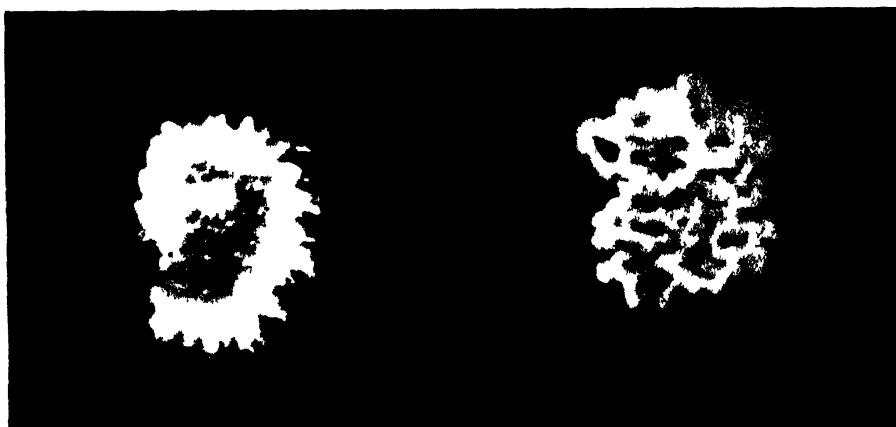
FIG. 5

Enzymes.	Organism.	Acts upon
Invertase and maltase	*Sacc. cerevisiae*	*Maltose*, saccharose, glucose, fructose, and mannose
Invertase, maltase, and melibiase	*Sacc. Carlsbergensis*	Raffinose, maltose, saccharose, glucose, fructose, and mannose
Invertase, lactase, and inulinase	*Sacc. fragilis*	*Lactose, inulin*, saccharose, glucose, fructose, galactose, mannose, and raffinose
Invertase, maltase, melibiase, trehalase, and dextrinase	*Sacc. Logos*	*Trehalose, dextrin*, saccharose, maltose, glucose, fructose, galactose, mannose, and raffinose

Although *S. Logos* in the above table is seen to be able to hydrolyse and ferment dextrin, yeasts do not contain amylases and therefore cannot attack starch or polysaccharides. The moulds are far more catholic than yeasts in these respects and are, indeed, veritable portmanteaux of enzymes, fully equipped to deal with almost anything. They are able to break down polysaccharides, starches, and protein; in many cases they also possess fat-splitting lipases, and can, of course, deal with all the sugars which the various yeasts are able to hydrolyse.

There is no little confusion about the enzymic properties of unicellular organisms; some, depending upon the collection from which they are drawn, show different activity from others which are supposedly identical. Reference will, however, be made to this later and some light will be thrown on the probable cause of these divergencies.

Of the enzymes associated with single cell organisms, some appear to act at the surface, others are regarded as diffusing out from the cell, although there is, indeed, very little evidence of this, whilst others are far less accessible and only come into play when the cell is ruptured. A simple example of a marked difference of this kind is to be found with ordinary yeast, in which the enzyme invertase is extremely active towards a cane sugar solution, resolving it to glucose and fructose without detriment to the cell structure, whereas, under similar conditions, the maltase of the yeast cell remains inactive towards maltose, being unable to get at it; maltose is only resolved to glucose when the yeast cell is ruptured and the enzyme freed.

A further point of interest here is that a yeast having a low invertase activity may, through appropriate propagation, for example, in a medium rich in cane sugar, become extremely invertase-active, particularly if the propagation is carried through a number of generations. The following results, taken from the work of E. R. Dawson, provide an example of this kind and show also that in a similar way a yeast of low maltase activity may be brought to a relatively high degree of maltase activity by appropriate propagation in a maltose-rich medium. It is not suggested, however, that this is the normal or the only way of influencing the enzymic activity of a yeast, but it serves to illustrate the comparative ease with which enzymic activity may be attained through external influences. It should be understood, when considering the following figures, that the units for invertase activity are larger than those for maltase activity and that in developing increased maltase activity different methods and different media are employed from those adopted when developing increased invertase activity, so one should not compare the figures for the one with those for the other; they show, however, marked increase in the activity of the enzymes concerned as the propagation proceeds.

Yeast.	Invertase activity.	Maltase activity.
Seed used..	1·8	0·9
After 5 multiplications	3·0	1·8
,, 25 ,, ...	5·9	2·5
,, 125 ,, ...	6·6	—
,, 650 ,, ...	7·9	—

It seems that, by calling these enzymes into play through environmental influence, either they become more active or their quantity in the cell is increased. Cases have been observed where the initial enzymic activity of the cells is so low and ultimately becomes so high as to suggest that the cell is able to provide itself with such enzymic powers as will enable it to live under widely different conditions on widely different media. Clearly, yeast brought up on one medium may behave differently from a yeast brought

up on another.   It is doubtful whether in biological work sufficient regard is paid to these strong environmental influences on yeast and on other unicellular organisms.

Attempts to produce in a yeast some new enzymic power different from those initially possessed have so far failed, except, perhaps, in the case of enzymes capable of resolving galactose.   For example, one has not yet succeeded in detecting maltase activity in *S. Marxianus* or in *S. exiguus*.   This may be due to the right conditions not having been found or to the propagation not having been carried sufficiently far under the most favourable conditions.   However, some measure of success in this direction has attended the work of Armstrong, Slator, and Harden, who, employing a yeast which initially possessed no measurable power of fermenting galactose, eventually induced it to show such activity by bringing it up in the presence of galactose.   Whether this is actually a case of creating new power for new cells, or whether it is a general calling into play of otherwise dormant powers, is difficult to say : the case seems clear in so far as new cells are concerned, although the latter explanation seems the more probable in view of the relationship between yeasts and moulds and the diverse enzymic powers which the latter show.   It will suffice, however, to stress here the importance in biochemical work of knowing the past history of the biological materials with which one works; it is insufficient to work merely with a specific organism—if the work is to be of value, one has to know a great deal about the past history of the organism since it was at the single cell culture stage.

With regard to oxidative–reductive systems of unicellular organisms, frequently referred to as the oxidase–reductase system, there seem to be two lines of thought, with but little experimental evidence upon which to base any definite ideas.   In the one case, the assumption is made that there are two definite and independent systems at work, the one oxidative, the other reductive, linked by the cytochrome of the cell; cytochrome being widely distributed in the cell in an oxidised form or in a reduced form.   The other view is based upon the idea of the functioning only of a reductive system of the cell itself through the activation of hydrogen.   This involves the conception of some cell substance activating hydrogen in certain circumstances, causing a transfer of hydrogen to a hydrogen acceptor, or causing a transfer of oxygen from an oxygen donator, and in that way being responsible for both types of change generally referred to as biological reduction and biological oxidation; terms which seem necessary in order to distinguish these changes, which, in the presence of the living cell, proceed easily, from the more usual reduction and oxidation processes of chemistry, which proceed with comparative difficulty.   The latter hypothesis, namely, that of hydrogen activation, has the merit of being simpler than that calling for independent oxidative and reductive systems and is supported by rather more evidence and, moreover, seems to meet equally well all the cases which have been studied.   Recently, too, W. G. Bennett has shown that the existence of an oxidative system, in addition to the reductive system postulated in the former scheme, is extremely doubtful.   He has shown that a yeast may be prepared, having the normal oxygen absorption powers, which will not exhibit the indophenol oxidase reaction.   If, however, a very minute trace of copper be added, something of the order of a few parts per million, then the indophenol oxidase reaction becomes evident in some cases, but not in all.

One is tempted to ask whether quite a number of these biochemical activities are not due to traces of inorganic substances and whether, indeed, some biological processes themselves are not dependent upon the presence of mere traces of inorganic agents acting directly or indirectly through subtle combinations with organic materials.   As an example of this, one calls to mind the part played by magnesium in the chlorophyll system.

When examining the vitamin value or vitamin activity of unicellular organisms, a similar state of affairs is found to exist as with the enzymic activity.   Here, again, although nothing very definite is known, there is a considerable body of evidence showing that vitamin potency may be dependent to a marked extent upon the vitamin potency of the medium in which the organism has been grown.   There are cases where bacteria are believed to fabricate their own vitamins : there are cases, for example, that of *Sacc. Logos*, where, as shown by J. C. Drummond and Whitmarsh, the balance of evidence points to the probability that this yeast is able to synthesise its own vitamin B.   Generally speaking, however, one may say the vegetable kingdom is the chief source of vitamins;

in plants they are fabricated and passed on to the animal kingdom to play their part in cell metabolism. It is interesting, therefore, to find amongst yeasts cases both of vitamin fabrication and of vitamin acquisition.

In so far as vitamin B is concerned, yeasts seem to be in the main dependent upon the medium in which they are grown for their vitamin B potency. In any case, a yeast of low vitamin B value may be changed to one of high vitamin B value by growing it through appropriate stages in a special extract of grain material. Whether the same applies to other cases of vitamin activity is not certain, but one knows of entirely different circumstances in which vitamin potency may be changed. There are, however, other, less direct, ways of changing vitamin potency; for example, a unicellular organism propagated under one set of conditions may have a very low ergosterol content, whilst if propagated in the same kind of medium but under different conditions of nutrition, it may be very rich in ergosterol, which is the precursor of vitamin D, being changed to that vitamin when brought under the influence of ultra-violet irradiation. In this particular instance, the essential points of difference seem to be an abnormal condition of oxygenation and an abnormal condition of nitrogen feeding. The ergosterol content of yeast prepared in accordance with the procedure worked out by Bennett may be raised from, say, 0·4% calculated on dry matter, to well over 1%, say 1·5%, calculated on the same basis. This appears to be a case of synthesis brought about by changed nutritional conditions and is of considerable interest when taken in conjunction with the observations in the case of vitamin B.

Coming to the question of the protein content of the cell, one may well consider how this complex molecule gets within the confines of the cell wall. A considerable amount of work has been done on the proteolytic enzymes of bacteria and of yeast, but generally from the point of view of understanding the degradation of the protein complex, not from the point of view of its upbuilding. There is, however, much uncertainty regarding the evidence brought forward, owing to the difficulty of interpreting the results and also from the almost complete disregard by many workers of the important influence which the concentrations of salts and of sugar exert on the cell membrane; likewise, the degree of acidity or alkalinity of the medium employed; all, or any, of which may promote or hinder osmosis. The opinion is fairly widely held that protein is broken down in two stages, first to amino-acids by some extra-cellular proteolytic enzyme; the second stage, namely, the subsequent resolution of the amino-acids, by some endocellular oxidation process. That is to say, in the case of yeast activity, the protein is first resolved to amino-acids by an extra-cellular enzyme and the amino-acids are then resolved further by an endocellular agent.

Examining changes of this kind in the reverse order, from the point of view of the cell itself, what it does, what it consists of, and from what it builds up its protein, helps one to accept or reject some of the current ideas. It is known that yeast cells contain 6—10% of nitrogen, calculated on dry matter, and that this is present in protein built up from simple inorganic or organic nitrogenous matter through enzymic agency. It is difficult to regard this process as taking place first by means of an endocellular enzyme building up the amino-acids and then, subsequently, an extra-cellular enzymic process completing the protein complex. In the case of yeast it seems the more likely that this synthesis takes place in some way through the agency of the cell wall : at any rate, a small amount of nitrogen is always excreted during protein synthesis by yeast. The protein is generally located within the cell, but under some conditions of growth, regarded as quite abnormal, protein may be formed on the exterior surface of the cells themselves.

The general mechanism of the synthesis of yeast protein seems to be one probably between the carbohydrate (glycogen) reserve and simple ammonia, amino- or amide groupings. Different kinds of nitrogen are made use of differently and it is known that a source of carbon is always simultaneously necessary. Under conditions where nitrogen is present at the same time as ammoniacal salts, as amino-acids and as polypeptide nitrogen, it has been found that about 97% of the ammoniacal nitrogen is utilised, about 60% of the amino-acids, and about 30% of the polypeptide nitrogen. If the nitrogen supply is in the form of amino-acids, its utilisation is associated with the utilisation of sugar, and

free oxygen is unnecessary. If, however, the nitrogen supply is in the form of inorganic salts, as urea, or as acid amides, then alcohol or organic acids are needed at the same time, together with a liberal supply of free oxygen, such as is provided during intensive aeration. So far as is known, the more complex forms of organic nitrogen, with the exception of simple polypeptides, are not utilised in any circumstances.

Under proper control, and given the right conditions—and they are very exacting—one may readily convert nitrogen of the air in the form of ammonium salts into protein on a large scale; in fact, it is the basis of industrial yeast production at the present day.

For example, in the manufacture of 10,000 kg. of fresh yeast, representing, say, 2700 kg. of dry matter, there may be used about 250 kg. of inorganic nitrogen in the form of ammonium salts of one kind or another, from which are recovered about 1300 kg. of dry full-protein. This, of course, does not represent the total quantity of protein contained in the total quantity of yeast cell substances, because, in addition to the 1300 kg. of full-protein referred to, a certain amount is also formed from organic sources of nitrogen present in the fermenting mash. It is necessary to bear in mind that these high conversions of inorganic nitrogen in the form of ammonia into organic forms of nitrogen as full-protein are only possible with certain races of yeast, and even then it is largely dependent upon the previous upbringing of the yeast used as seed for the fermentation.

Processes of this kind not only are of considerable scientific and industrial interest, but might be of great economic importance to the country, particularly in time of scarcity. Reference has been made to these facts elsewhere, but it may be pointed out that a yeast factory producing, say, 200 tons of bakers' yeast per week is producing about 27 tons per week of dry protein and 4 tons of fat. Put into terms of a better-known form of protein—namely, beef—and making allowances for bones, hide and other non-edible parts, this means the conversion of nitrogen from the air, through ammonia, into protein at the rate of some 500 bullocks per week at a cost not widely different from the cost of raising beef in this country on the basis of its food value.

Much attention has been given to the study of the fixation of nitrogen by soil organisms since the early observations of Jodin that mineral salts as well as carbohydrates play an important rôle. But little is known regarding the factors which regulate the nitrogen intake of organisms, or how yeast, which contains so large a proportion of protein within its cell wall, builds up complex nitrogen-containing compounds from simple ammonia.

Of the other well-known constituents of the cell, namely, carbohydrate and fat, it is known that the cell stores within the confines of its membrane a reserve of carbohydrate as glycogen accompanied by mannan, the latter probably constituting the main portion of the cell membrane. Glycogen seems to be the reserve from which is drawn the carbon necessary, not merely for the fabrication of the cell wall, but also, as has already been mentioned, for the synthesis of protein and for the building up of fat and ergosterol. This central store of carbohydrate is very labile, being readily disintegrated when the cell is introduced into media rich in sugar, but is gradually built up again, thus replenishing the store as the amount of sugar available declines. When a heavy demand is made upon this reserve of carbohydrate for any one purpose, for example, in protein synthesis, less remains for fat or ergosterol formation. Therefore, in growing yeast, for instance, to contain a high proportion of ergosterol, care must be taken to keep the nitrogen supply at a minimum.

With this carbohydrate store is also associated the storage of inorganic constituents such as phosphate and potassium. Large utilisation of the carbohydrate store for protein synthesis is thus inimical to the storage of potassium. Far more complex processes seem to be involved when one comes to the question of the storage of phosphates within the cell. Phosphates and magnesium salts are utilised in proportion to their concentration, whether owing to mass-action or through osmosis is not known. These questions are extremely complicated, the influences at work are interdependent and their balance easily disturbed. Comparatively slight changes of environment may lead to marked changes in the physical properties, the chemical constituents, and the chemical activity of the cells concerned.

There are, of course, many other important constituents of the cell; for example,

sulphur for cystine and glutathione formation, and iron for cytochrome formation;· these are present only in small quantities. Zinc is often found in yeast in unexpected amounts, but this may arise from assimilation of zinc contained in the mash materials and be without any functional significance.

In conclusion, however, reference may be made to " bios," as several investigators are endeavouring to ascertain the nature of this mysterious growth-promoting factor. Very little is known definitely, but from observation on single cell behaviour, it is recognised, in a general way, that " bios " influences cell multiplication, promoting budding rather than an increase in the size of the cells. Whereas carbohydrate and nitrogen, together with the necessary inorganic salts, seem to influence cell size rather than cell multiplication, nitrogen seems also to influence the general appearance of the cell protoplasm regardless of the size of the cells concerned.

It is only possible within the scope of this communication to refer to some of the more important aspects of cell fabrication and of cell properties. The whole question of the chemistry of unicellular organisms, particularly of yeast, calls for most careful study. A better understanding of the processes involved will throw much needed light on the more complex problems and the larger issues of animal and vegetable nutrition. The feeling grows that chemistry would profit from a closer study of biological phenomena and that biochemistry is in need of more chemistry.

46. *The Parachors of Ethyl Orthoformate and Triphenylmethane.*

By DALZIEL LL. HAMMICK and HAROLD F. WILMUT.

WE recently showed (J., 1934, 32) that the parachors of tetrabromo- and tetranitro-methane have negative anomalies of $-16\cdot7$ and $-20\cdot8$ respectively. From data given by Przyluska (*J. Chim. phys.*, 1909, **7**, 518), the parachor for triphenylmethane was derived as 578, $P_{calc.}$ being $591\cdot9$, and the suggestion was made that the presence of the three large groups substituted in the methane molecule was connected with the anomaly. A determination of the parachor of ethyl orthoformate showed, however, that for this trisubstituted methane no anomaly exists ($P_{obs.} = 367\cdot2$; $P_{calc.} = 367\cdot2$), and led us to redetermine the parachor of triphenylmethane. We find $P_{obs.} = 586\cdot5$ ($P_{calc.} = 591\cdot9$), there being no anomaly greater than the 1% variation allowed by Sugden's method. There is thus at present no evidence for parachor anomaly in the trisubstituted methanes.

Surface tensions were determined by Sugden's " bubble pressure " method, the apparatus being standardised with pure benzene. Densities were found by means of a standardised dilatometer.

Ethyl orthoformate, b. p. $145\cdot1°$.					Triphenylmethane, m. p. $92\cdot8°$.			
Temp.	$d_4^{t°}$.	γ, dynes/cm.	$P_{obs.}$		Temp.	$d_4^{t°}$.	γ, dynes/cm.	P_{obs}
25·0°	0·888	23·41	366·7		98·6°	1·0133	35·10	586·2
40·0	0·872	21·99	367·6		108·2	1·0058	34·22	586·9
50·0	0·862	20·90	367·0		117·6	0·9986	33·15	586·2
60·0	0·851	19·99	367·7		128·4	0·9908	32·25	586·9

Mean $P_{obs} = 367\cdot2$; $P_{calc.} = 367\cdot2$.   Mean $P_{obs.} = 586\cdot5$; $P_{calc.} = 591\cdot9$.

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47. *The Decomposition of Acetyl Peroxide.*

By O. J. WALKER and G. L. E. WILD.

IN the discussion of the anode reactions taking place during the electrolysis of organic acids or their salts, the theory of the intermediate formation of peroxides and per-acids has played a prominent part, largely due to the work of Fichter and his co-workers. This theory (known as the " peroxide theory ") is based mainly on the qualitative similarity

between the products formed at the anode during the electrolysis of any given acid and the products of the thermal decomposition of the corresponding acyl peroxide or peracid. In many cases, however, the quantitative composition of the products is very different in the two processes. In particular, it has been shown (Walker, J., 1928, 2042) that the thermal decomposition of acetyl peroxide, both in the pure state and in solution, does not consist mainly of a reaction according to the simple equation $(CH_3 \cdot CO \cdot O)_2 = 2CO_2 + C_2H_6$ (1); methane is always formed, and the only circumstances in which the peroxide breaks up with any approach to the stoicheiometric proportions of equation (1) appears to be when it is exposed at the ordinary temperature to ultra-violet light; *e.g.*, in one such experiment a $CO_2 : C_2H_6$ ratio of 2·9 : 1 was obtained (Walker, *loc. cit.*, p. 2044). A more detailed investigation of this reaction is being undertaken.

As regards the thermal decomposition, however, it still seems to be assumed by supporters of the peroxide theory that if acetyl peroxide could be made to decompose at a sufficiently low temperature it would break up more nearly in accord with equation (1). On the other hand, comparison of the results of the explosive decomposition · (Fichter and Krummenacher, *Helv. Chim. Acta*, 1918, 1, 152) with those of the above-mentioned experiments, which were carried out at about 80°, suggested that less ethane would be formed at even lower temperatures. Since no experimental evidence was available, the nature of the gaseous products obtained by heating liquid acetyl peroxide at temperatures between 30° and 90° was investigated, and the above deduction confirmed.
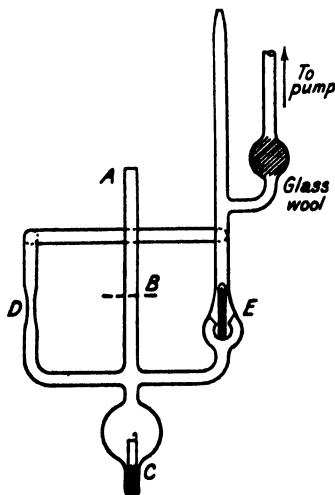
EXPERIMENTAL.

The white crystalline peroxide, prepared by Gambarjan's method (*Ber.*, 1909, 42, 4010), was recrystallised from ether. As the peroxide vapour readily attacks rubber and mercury, an all-glass apparatus was used (see fig.). After the peroxide, contained in a small glass tube, had been introduced through *A*, the apparatus was sealed off at *B*, evacuated through the Töpler pump, and the constriction *D* sealed, the bulb containing the peroxide being cooled with solid carbon dioxide during these operations.

The surrounding thermostat (not shown) was then slowly brought to the required temperature and maintained thereat ($\pm$ 1·0°) until a sufficient quantity of gas (at least 10 c.c. measured at ordinary temperature and pressure) had been formed. The average rate of evolution of gas, in c.c. per hour, decreased rapidly at first, and then very slowly from about 14·0 at 90° to 0·2 at 30°. The bulb *C* was then cooled and, after the septum at *E* had been broken with the usual magnetic arrangement, the whole of the gas was collected through the Töpler pump. A portion of it was then transferred to a Bone and Wheeler apparatus, in which the carbon dioxide, oxygen, ethylene, and carbon monoxide were determined by absorption in the usual manner. The methane and ethane were determined by the fractional condensation method using liquid air (Walker and Shukla, J., 1931, 368) in order to confirm the presence of these two hydrocarbons independently of one another. The separated portions of the hydrocarbon residue gave C/A ratios on explosion very close to 2·00 and 1·25, *i.e.*, the theoretical values for these two gases respectively.

Results.—The composition of the gaseous products (in % by vol.) is shown in Table I. It will be seen that the amount of ethane becomes less with decreasing temperature, until it is only about 2% of the volume of methane formed.

TABLE I.

Temp.	30°.	45°.	55°.	70°.	80°.	90°.
CO_2, % by vol.	59·5	64·0	55·5	58·4	62·2	62·0
O_2 ,, ...	1·9	1·3	0·8	0·9	0·7	1·1
C_2H_4 ,, ...	0·5	0·4	0·3	0·1	0·7	0·1
CO ,, ...	1·9	1·1	1·6	1·0	1·0	0·8
C_2H_6 ,, ...	0·7	0·7	1·4	3·7	3·0	8·8
CH_4 ,, ...	35·4	32·3	40·0	35·9	32·2	27·1

A decomposition of the peroxide according to equation (1) is therefore not favoured by allowing the reaction to take place as slowly and at as low a temperature as possible. The results described in this and in the previous paper show that when acetyl peroxide is heated under a wide variety of conditions, both alone and in solution, methane and carbon dioxide are the main gaseous products. The formation, in the absence of solvent, of a considerable amount of a gum-like residue suggests a rather complex decomposition process in which poly-merisation of simpler primary products occurs. In a few experiments upon the residue from the incompletely decomposed peroxide, no evidence was found for the formation of formaldehyde, peracetic acid, or acetic acid, which might accompany the methane according to Fichter and Panizzon's suggestion (*Helv. Chim. Acta*, 1932, **15**, 1007). Since, however, we have been concerned mainly with determining the effect of lower temperatures upon the formation of ethane, we have not attempted a complete investigation of the residue.

Discussion.—If acetyl peroxide is formed at the anode during the electrolysis of acetate solutions, then the conditions must be particularly favourable to the decomposition into $C_2H_6 + 2CO_2$, for in this case appreciable amounts of methane are formed only under very limited conditions of low current density and high concentration of acetate (cf. Shukla and Walker, *Trans. Faraday Soc.*, 1932, **28**, 457; also Fichter and Panizzon, *loc. cit.*). It does not appear likely that this is due to catalytic influence of the electrode surface, because Wieland and Pascual-Vila (*Annalen*, 1926, **446**, 60) found that the decomposition of acetyl peroxide in the presence of platinum under various conditions does not give ethane and carbon dioxide.

Finally, it is of interest to compare the gaseous products of the decomposition of acetyl peroxide with those of two other reactions in which the intermediate formation of this peroxide has been assumed, *viz.*, (i) the action of barium peroxide on acetic anhydride, and (ii) the oxidation of acetic acid with persulphates.

(i) This reaction was that actually used by Brodie (*Phil. Trans.*, 1863, **153**, 413) in his original preparation of acetyl peroxide, and for this purpose the temperature must be kept low. At higher temperatures a vigorous reaction takes place, and Schützenberger (*Compt. rend.*, 1868, **61**, 487) stated that a gas composed exactly of two volumes of carbon dioxide and one volume of a hydrocarbon having the character and composition of $2CH_2$ was evolved. This result has apparently never been confirmed, though often quoted as a method of preparing ethane (cf. Armstrong, *Nature*, 1934, **133**, 379). On the contrary the work of Darling (*J.*, 1868, **21**, 500), of Fichter (*Z. Elektrochem.*, 1914, **20**, 473), and of Glasstone and Hickling (*Chem. and Ind.*, 1934, 512), in which barium peroxide and acetic anhydride were heated together under a variety of conditions, with and without the addition of water, shows that in every case little ethane and considerable quantities of methane are obtained. A comparison of the data of these investigators with the composition of the gas obtained by heating the peroxide alone (this paper and Walker, *loc. cit.*) shows that there is very close qualitative, and in some cases quantitative, resemblance in the gaseous products. To make the results more comparable, the gas compositions given in Table II are referred in each case to 100 vols. of methane, since in some cases the carbon dioxide was not determined and in others no ethane was found.

TABLE II.

Reaction.	Observers.	Composition (by vol.) of gaseous products ($CH_4 = 100$).		
		CH_4.	C_2H_6.	CO_2.
Decomp. of $(AcO)_2$:				
(a) liquid	W. & W.	100	2·0—32·5	139—229
(b) in aq. soln.	W.	100	5·8—14·4	360—475
	D.	100	24·3	Not measured
BaO_2 and Ac_2O	F.	100	16·5	255
	G. & H.	100	50·8	549
AcOH and $Na_2S_2O_8$	G.	100	0—30·5	Not measured
	F. & P.	100	0	489

W. & W. = Walker and Wild; W. = Walker; S. = Darling; F. = Fichter; G. & H. = Glasstone and Hickling; G. = Gordon; F. & P. = Fichter and Panizzon.

(ii) The reaction between acetic acid and sodium persulphate in aqueous solution has been investigated by Gordon (*J. Physical Chem.*, 1914, **18**, 55) and by Fichter and

Panizzon (*loc. cit.*, p. 996). The latter authors consider the first step in the reaction to be the oxidation of acetic acid to acetyl peroxide, and they attribute the fact that more methane than ethane is formed (see Table II) to hydrolysis of the peroxide to peracetic acid, since they assume that acetyl peroxide itself does not give methane as one of its primary decomposition products. In the light of the evidence now put forward, however, the products obtained in the oxidation of acetic acid appear to be such as are normally obtained from the decomposition of acetyl peroxide.

We conclude, therefore, that the reaction (1) is not the main process taking place when the peroxide is decomposed either directly or in reactions in which its intermediate formation appears likely.
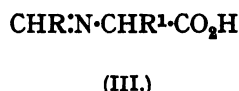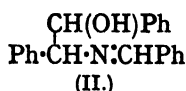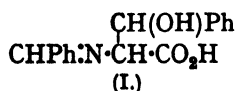
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48. *Equilibria between Amino-acids and Aromatic Aldehydes. Part I.*

By J. MASSON GULLAND and THOMAS H. MEAD.

THE extensive use of Sörensen's method of " formol titration " of amino-acids, peptides, and proteins (*Biochem. Z.*, 1907, **7**, 45) has led many chemists to study the nature of the equilibria existing in aqueous solutions of formaldehyde and these substances, but analogous equilibria between aromatic aldehydes and amino-acids have received little attention.

Erlenmeyer and his collaborators (*Annalen*, 1894, **284**, 36; 1899, **307**, 79, 113; 1904, **337**, 212, 307) showed that benzaldehyde (2 mols.) condensed with glycine (1 mol.) in presence of sodium hydroxide (2·5 mols.) to yield the sodium salt of *N*-benzylidenephenyl-serine (I) and the non-acidic *N*-benzylidene derivative of αβ-diphenylhydroxyethylamine (II). Erlenmeyer and Bade (*ibid.*, 1904, **337**, 222) found that *o*-methoxybenzaldehyde readily underwent similar transformations with glycine, although anisaldehyde, *p-iso*-propylbenzaldehyde, salicylaldehyde, vanillin, and piperonal reacted only very slightly. Phenylalanine (*ibid.*, p. 215), tyrosine, aspartic acid, and leucine (Erlenmeyer, *Ber.*, 1897, **30**, 2896) reacted with benzaldehyde to give only the benzylidine derivative (II) and none of the sodium salt corresponding to (I).

$$
\begin{array}{ccc}
\text{CH(OH)Ph} & \text{CH(OH)Ph} & \text{CHR:N·CHR}^1\text{·CO}_2\text{H} \\
\text{CHPh:N·CH·CO}_2\text{H} & \text{Ph·CH·N:CHPh} & \\
\text{(I.)} & \text{(II.)} & \text{(III.)}
\end{array}
$$

Gerngross (*Biochem. Z.*, 1920, **108**, 89) and Gerngross and Zühlke (*Ber.*, 1924, **57**, 1482) obtained the sodium salts of *N*-arylidene derivatives of amino-acids (III) by interaction of the aldehyde with the amino-acid ester in presence of sodium ethoxide, and showed that these salts are hydrolysed by water into the aldehyde and amino-acid. Bergmann, Ensslin, and Zervas (*Ber.*, 1925, **58**, 1034) and Bergmann and Zervas (*Z. physiol. Chem.*, 1926, **152**, 282) prepared Schiff's bases (III) by condensing benzaldehyde, salicylaldehyde, furfur-aldehyde, *p*-nitrobenzaldehyde, and chloral with a representative selection of α-amino-acids in presence of baryta, barium acetate, or brucine or other alkaloids.

Apart from the interest of the equilibria involved, we decided to investigate the nature of these reactions partly because of the divergences reported above and partly because the progress of other researches demanded a knowledge of the relative capacities of aromatic aldehydes for condensation with amino-acids, in which Erlenmeyer and Bade (*loc. cit.*) had found marked variations.

First, Erlenmeyer's observations on the interaction of benzaldehyde and glycine were confirmed, and phenylserine, αβ-diphenylhydroxyethylamine, and their benzylidene derivatives (I and II) were isolated as described by him.

Secondly, repetition of the work of Bergmann and his collaborators confirmed that glycine condenses with benzaldehyde and with salicylaldehyde in presence of baryta and barium acetate respectively to yield the barium salts of the corresponding Schiff's bases.

In addition, the barium salts of 2-hydroxy-3- and -5-methoxy-N-benzylideneglycine and of their 2-methyl ethers (all of type III) were prepared by similar methods.
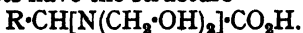
In contrast to these results, protocatechualdehyde, its two monomethyl ethers, its dimethyl ether, and *p*-dimethylaminobenzaldehyde all failed to yield sparingly soluble barium salts when treated with glycine and barium hydroxide or acetate, and were recovered unchanged.

It was thus evident that there is no discrepancy between the results of Erlenmeyer and those of Bergmann, and that the nature of the product in reactions of this type is influenced by the conditions prevailing. On the other hand, further investigation was required of the fact that some aromatic aldehydes appear to condense with amino-acids, whereas others do not.

There are two major objections to employing the isolation of the products of condensation to investigate the equilibria between aldehydes and amino-acids. Failure to isolate a compound might be due solely to its greater solubility, and if in different examples the solubilities of the products were not the same, the yields would bear no relation to the affinities for condensation, because the active concentration of the products would become constant when precipitation occurred, and the reactions would then cease to be true equilibria.

Holden and Freeman (*Austral. J. Exp. Biol.*, 1931, **8**, 189) used the van Slyke method to estimate the decrease in amino-nitrogen during the condensation of formaldehyde with amino-acids. This procedure was unsuccessful in experiments with aromatic aldehydes, because hydrolysis of the Schiff's bases occurred in the acetic acid required in the method.

Polarimetric investigation of the reactions offered the great advantages of continuous examination of their progress and the absence of disturbance of the equilibria when these were established. Holden and Freeman (*loc. cit.*) observed only small changes in the optical activity of amino-acids in presence of formaldehyde and alkali, a fact which is in harmony with Levy's conclusion (*J. Biol. Chem.*, 1933, **99**, 767) that the products have the structure

$$R\cdot CH[N(CH_2\cdot OH)_2]\cdot CO_2H.$$

FIG. 1.

Solutions containing 0·125 millimol. of each of d-phenylalanine, sodium hydroxide, and dimethoxybenzaldehydes.

With aromatic aldehydes, on the other hand, large changes in rotation take place, as is described below.

The use of the polarimetric method imposed certain restrictions. With very few exceptions, condensations between aldehydes and amino-acids only occur in alkaline media. Moreover, the specific rotations of amino-acids vary widely with the p_H of the solutions owing to differences between the optical rotatory powers of the " zwitterion," anion, and kation. This necessitated control of the alkalinity of the reaction mixtures, and attention has been restricted in the first instance to 2 : 3-, 2 : 5-, and 3 : 4-dimethoxybenzaldehydes, since the use of acidic phenolic aldehydes would have introduced complications difficult to control. The first two aldehydes condensed readily with barium aminoacetate; the last did not appear to do so. *d*-Phenylalanine was selected as the amino-acid, since it is moderately soluble, has a relatively high specific rotation ([α]$_D$ + 35°) which is still measurable in alkaline solutions, and is readily prepared synthetically (Harington and McCartney, *Biochem. J.*, 1927, **21**, 852; Lamb and Robson, *ibid.*, 1931, **25**, 1231; Fischer and Schoeller, *Annalen*, 1907, **357**, 1). 50% Ethyl alcohol was the most suitable solvent, and since buffer-

ing could not be satisfactorily effected in this, approximately constant conditions were realised by the use of one molecular proportion of sodium hydroxide.

The observed rotations of mixtures of equimolecular proportions of *d*-phenylalanine, sodium hydroxide, and 2 : 3-, 2 : 5-, or 3 : 4-dimethoxybenzaldehyde in 50% alcohol increased ultimately to a constant value (Fig. 1); equilibrium was more rapidly attained with the first two aldehydes than with the third. Hence, in alkaline solution *d*-phenylalanine combined with the aldehydes to yield compounds of high specific rotation; but no other conclusions could be drawn, since the values of these rotations were unknown and could not be directly determined. Even if the products could have been isolated in pure state, and attempts to do this were unsuccessful, they would have decomposed in solution owing to alterations of the conditions of equilibrium (cf. Gerngross and Zühlke, *loc. cit.*). Approximate values of the observed and specific rotations of the condensation products were obtained indirectly as follows. Fig. 2 shows the observed rotations of solutions of *d*-phenylalanine at equilibrium with 1 mol. of sodium hydroxide and various molar proportions of the three aldehydes. In each case the rotation rose on the addition of more

FIG. 2.
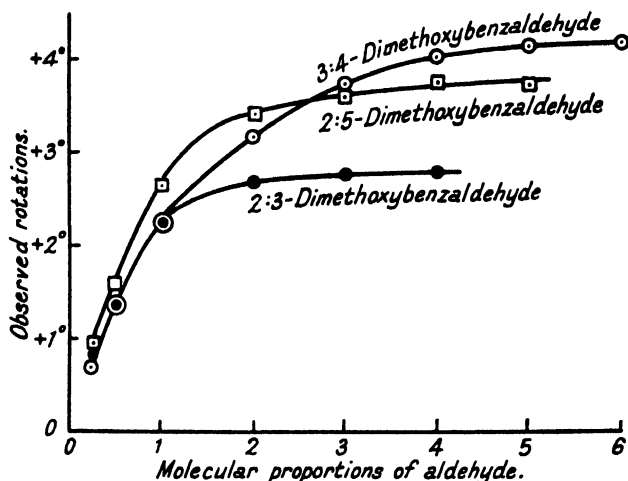
Rotations of solutions containing d-*phenylalanine* (0·125 *millimol.*) *at equilibrium with varying proportions of dimethoxylbenzaldehydes.*

aldehyde, owing to closer approach of the equilibrium to complete condensation. On the probable assumption (see below) that the rotations are modified but slightly and to the same extent by the presence of the uncombined excess of the aldehydes, the maximum rotations obtained by extrapolation of the curves have been taken as approximate values of the observed rotations of the reaction products under the conditions of the experiments.

These deductions are only valid so long as the reactions remain as reversible equilibria. If, *e.g.*, any appreciable amount of arylidene derivative of diarylhydroxyethylamine (as II) were formed, as might happen by analogy with Erlenmeyer's work, the observed rotation would be lower, since these bases are optically inactive when formed in this way. This question was examined as follows. Solutions containing 1 mol. each of *d*-phenylalanine and sodium hydroxide and 3 mols. of the aldehyde were allowed to attain equilibrium, and were then adjusted to p_H 4 with acetic acid in order to hydrolyse the condensation product. The observed rotations fell to the same value, which was also the same, within the limits of experimental error, as that observed with solutions at p_H 4 which contained all the reactants but had not been allowed to become alkaline at any stage. This value was very slightly higher than the observed rotation of the *d*-phenylalanine alone at p_H 4, the difference being due presumably to the influence of the uncombined aldehyde in the solution. In the same series of experiments, the aldehyde and amino-acid were separated quantitatively, and were recovered as 2 : 4-dinitrophenylhydrazones and as α-naphthyl-

carbamyl or *p*-toluenesulphonyl derivatives respectively. No difference could be detected, in weights or purity of the materials recovered, between experimental and control solutions. It was concluded, therefore, that the reactions were true equilibria, and are thus unlike Erlenmeyer's reactions, the differentiating factor being the high concentration of sodium hydroxide used by him.

In the light of the experiments just described, comparable rate of reaction curves (Fig. 3) were obtained by plotting the rotations in Fig. 1 as percentages of the observed rotations of the corresponding pure condensation products as deduced by extrapolation of the curves in Fig. 2. It is evident that, under similar conditions, 2 : 3- and 2 : 5-dimethoxybenzaldehydes condensed both more rapidly and to a greater extent with *d*-phenylalanine than did the 3 : 4-isomeride, a conclusion which harmonises with the results of the experiments on the isolation of barium salts of Schiff's bases of glycine.

FIG. 3.
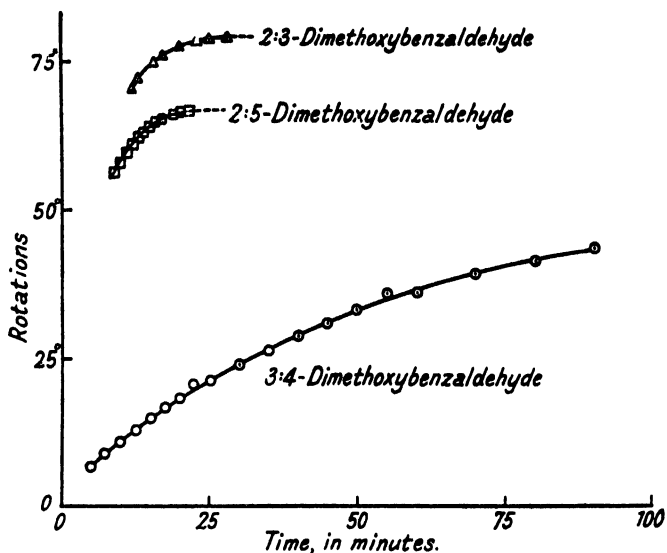
Rates of reaction between d-*phenylalanine and dimethoxybenzaldehydes Rotations are expressed as percentages of the values deduced for the corresponding phenylalanine–aldehyde compounds.*

The use of 50% alcohol as solvent allowed relatively high concentrations of the aldehydes to be reached, but no accurate control of the p_H was possible. Measurements were therefore made in buffered aqueous solutions at different p_H values, and Table I summarises the equilibrium rotations of buffered aqueous solutions of *d*-phenylalanine both alone and at equilibrium with 1 mol. of 2 : 3- and 3 : 4-dimethoxybenzaldehydes. Fig. 4 shows the results obtained at p_H 9·3 and 9·6. It is clear that in both cases reaction was slight at p_H 8, that the effect of increasing the hydroxyl-ion concentration was to raise both the rate of attainment of equilibrium and the extent of the condensation, and that here again the 2 : 3-isomeride condensed more quickly and to a greater extent than did the 3 : 4-isomeride. Table I also shows that the depression of the ionisation of the amino-group of phenylalanine becomes appreciable over the range p_H 8·5—10, and this is in harmony with the p_{K_a} values of monoaminomonocarboxylic acids. It is over this region also that the extent of condensation with the aldehydes increased greatly, and this implies that the aldehydes condense with the un-ionised amino-group of the amino-acid anion. This conclusion is in agreement with the views of others on the condensation of formaldehyde with amino-acids. The greater extent of condensation in the more alkaline solutions is presumably due to the higher concentration of undissociated amino-groups; the greater rapidity with which equilibrium is reached may possibly be attributable in part to hydroxyl-ion catalysis.

P

As regards the structure of the products of condensation, it is doubtful whether (VI) would account for the enhanced rotatory power, although (III), (IV), or (V) might do so.

$$Ar·CH(OH)·NH·CH{<}{CH_2Ph \atop CO_2H} \quad Ar·CH\left[NH·CH{<}{CH_2Ph \atop CO_2H}\right]_2 \quad [Ar·CH·OH]_2N·CH{<}{CH_2Ph \atop CO_2H}$$

$$\text{(IV.)} \qquad\qquad \text{(V.)} \qquad\qquad\qquad \text{(VI.)}$$
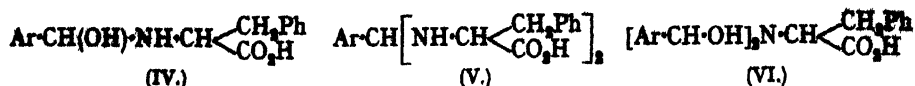
It is well known that double bonds in juxtaposition to an asymmetric atom, as in (III), increase its rotatory power. Further, the relationship between phenylalanine and (V) is not widely different from that between cysteine, with its small rotation, and cystine, with greatly increased optical activity. In addition, (IV) contains a new asymmetric carbon atom which might be optically active by analogy with the asymmetric synthesis of optically active hydroxynitriles in presence of alkaloids (Bredig and Minaeff, *Biochem. Z.*, 1932, **249**, 241). It is not possible to decide between these structures from polarimetric measurements. By using the slow-reacting 3 : 4-dimethoxybenzaldehyde in buffered aqueous solution, indications were obtained that the condensation involved 2 mols. of

FIG. 4.
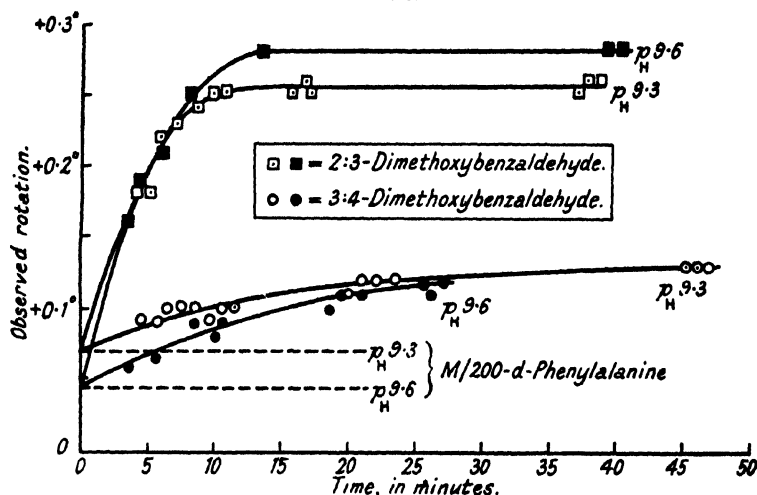
d-Phenylalanine and dimethoxybenzaldehydes in buffered aqueous solutions.

amino-acid and 1 mol. of aldehyde, but in general the reactions are too rapid to permit sufficiently accurate determinations, and retardation of the rate by dilution of reactants or lowering of temperature would introduce practical difficulties, such as small observed rotations and low solubilities of aldehydes. Possibly a decision on the structures might be reached by titration methods, as used by Levy (*J. Biol. Chem.*, 1933, **99**, 767) in the case of formaldehyde.

EXPERIMENTAL.

Schiff's Bases of Barium Aminoacetate.—(i) *Phenolic.* A solution of the aldehyde (3 g.; 1·5 mols.) in 50% alcohol (10 c.c.) was added to glycine (1 g.; 1 mol.) and barium acetate (3·0 g.) in warm water (6 c.c.) and kept over-night at 0°; if the product had not crystallised, the mixture was cooled further, and the material which separated was collected, washed with 50% alcohol and ice-water, dried in a vacuum desiccator, and stirred into dry ether to remove any free aldehyde.

Barium 2-hydroxy-3-methoxybenzylideneglycine was deposited in the reaction mixture as a yellow crystalline powder, which could be recrystallised from 50% alcohol, or better, by adding 2 vols. of acetone to the aqueous solution and cooling the mixture in ice. It formed canary-yellow, spherical aggregates of minute needles (Found : N, 5·0; Ba, 23·1. $C_{20}H_{20}O_8N_2Ba$ requires N, 5·1; Ba, 24·8%), which did not melt, and underwent hydrolysis when treated with acids or warm water.

The β-methoxy-salt was obtained as small, orange, hair-like crystals by cooling the reaction mixture in a freezing mixture. It was hydrolysed by warm water (Found : N, 5·0; Ba, 24·0. $C_{24}H_{22}O_8N_2Ba$ requires N, 5·1; Ba, 24·8%).

(ii) *Non-phenolic.* A mixture of the aldehyde (2·2 g.; 1 mol.) in 50% alcohol (12 c.c.), glycine (1 g.; 1 mol.), and barium hydroxide octahydrate (2·1 g.; 0·5 mol.) in water (4 c.c.) was warmed until it became clear, and then cooled. After some hours at 0°, the crystalline precipitate of the barium salt of the Schiff's base, which had separated slowly, was collected, washed with 50% alcohol and ice-water, dried in a desiccator, and finally washed with dry ether. The non-phenolic Schiff's bases are more readily hydrolysed than their phenolic analogues.

Barium 2 : 5-*dimethoxybenzylideneglycine* formed almost colourless, small, irregular plates, which were hydrolysed in cold water and decomposed partly when dried at 75° in a vacuum (Found : N, 4·8; Ba, 23·6. $C_{22}H_{24}O_8N_2Ba$ requires N, 4·8; Ba, 23·6%).

The 2 : 3-*isomeride* formed almost colourless plates, which became oily when washed with water, owing to partial hydrolysis (Found : N, 4·8; Ba, 25·3. $C_{22}H_{24}O_8N_2Ba$ requires N, 4·8; Ba, 23·6%).

Attempts to condense Certain Other Aldehydes with Glycine.—Vanillin. Experiments were made in similar conditions to those described above. With barium acetate, practically all the vanillin was recovered unchanged (m. p. and mixed m. p.). With barium hydroxide, faintly yellow, crystalline barium vanillin was isolated (Tiemann and Haarmann, *Ber.*, 1874, **7**, 615) (Found : Ba, 29·3. Calc. for $C_{16}H_{14}O_6Ba$: Ba, 31·2%), which yielded vanillin and barium sulphate when treated with dilute sulphuric acid.

isoVanillin. After an attempted condensation using barium acetate, about 75% of the *iso*vanillin used separated in pure condition when the mixture was left over-night at 0°.

Veratraldehyde. No precipitate was formed when barium hydroxide was used under the foregoing conditions, and on concentrating and cooling the solution, veratraldehyde separated. *p*-Dimethylaminobenzaldehyde also failed to condense in presence of barium acetate.

Rate of Reaction of d-*Phenylalanine with Dimethoxybenzaldehydes in 50% Alcohol in Presence of Sodium Hydroxide : Reactants in Molecular Proportion.—Solutions.* A 0·25N-sodium hydroxide solution in 50% ethyl alcohol, kept in hard glass and protected from carbon dioxide, remained of constant strength throughout the experiments. An aqueous solution of d-phenyl-alanine ($[\alpha]^{20°}_{5461} = + 37·4°$, $[\alpha]^{20°}_D = + 35·2°$, both in water) (0·2062 g. in 10·0 c c.; 1 c.c. = 0·125 millimol.) was prepared at frequent intervals; and absolute alcoholic solutions were prepared containing 0·0519 g of 2 : 3-, 2 : 5-, or 3 : 4-dimethoxybenzaldehyde in 2·5 c.c (1 c.c. = 0·125 millimol).

Procedure. The aldehyde solution (1·0 c c) was added rapidly to the phenylalanine solution (1·0 c.c) and sodium hydroxide solution (0·5 c c.), the time of addition being noted as the start of the experiment, and the solutions being at 20°; the resulting solution contained 0·125 millimol. of each reactant in 2·5 c c. of 50% alcohol, the slight contraction on mixing being neglected The solution was at once transferred to a 1-dm. polarimeter tube, and rotations observed at definite times. The results are given in Fig 1, four concordant experiments having been made with 3 : 4-dimethoxybenzaldehyde and two with each of the other two aldehydes.

In a control experiment in which absolute alcohol (1·0 c.c.) replaced the aldehyde solution, the observed rotation was 0·12°, this remained unchanged for 17 hours. Under the conditions of these experiments, therefore, the d-phenylalanine had $[\alpha]_{5461} = + 14·5°$. The mercury green line was used throughout this work.

Determination of the Specific Rotation of the Products of Condensation using Excess of the Aldehydes.—Solutions. The phenylalanine and sodium hydroxide solutions were those used in the preceding experiments. The aldehyde solutions were prepared by weighing into a graduated flask sufficient aldehyde to contain the desired molecular proportion in 1·0 c c. of alcoholic solution.

Procedure. Reaction mixtures containing 1·0 c.c. of each of the phenylalanine and aldehyde solutions and 0·5 c.c. of the sodium hydroxide solution were kept at room temperature over-night in stoppered flasks to allow them to reach equilibrium. The rotations were then measured in a 1-dm. tube, and again after some hours in order to ensure that equilibrium had been attained. The results are given in Fig. 2, and by extrapolation the following approximate values for the observed rotations of the condensation products from the isomeric dimethoxybenzaldehydes were obtained : 2 : 3-, + 3·0°; 2 : 5-, + 4·0°; 3 : 4-, + 4·3°. If it is assumed that condensation has proceeded to completion in presence of the large excess of the aldehydes, with the production of one of the substances (III), (IV), (V), or (VI), then the following would be the specific rotations of the sodium salts of these products respectively in 50% alcohol when formed from each of the

three dimethoxybenzaldehydes: 2 : 3-, + 192°, 181°, 126°, 121°; 2 : 5-, + 256°, 242°, 168°, 161°; 3 : 4-, + 276°, 258°, 180°, 173°.

Interaction between d-*Phenylalanine and Dimethoxybenzaldehydes in Buffered Aqueous Solutions.*—*Solutions.* Buffer solutions were prepared according to Clark (" Determination of Hydrogen Ions," 1920, p. 69, Williams and Williams, Baltimore).

The required aldehyde (0·0519 g.) was dissolved in 50·0 c.c. of buffer solution at the required p_H; 40·0 c.c. of this solution contained 0·0415 g. (0·25 millimol.) of aldehyde. d-Phenylalanine (0·0619 g.) was dissolved in 15·0 c.c. of buffer solution at the required p_H; 10·0 c.c. of this solution contained 0·0413 g. (0·25 millimol.).

Procedure. The aldehyde solution (40·0 c.c.) and phenylalanine solution (10·0 c.c.) were rapidly mixed, and the time noted as the start of the experiment. The mixture was quickly transferred to a 4-dm. polarimeter tube and polarimetric observations were begun at once. The p_H of the reaction mixture, determined colorimetrically before and after the reaction, remained constant.

The rotations of 0·005M-d-phenylalanine over the range p_H 7—10 were determined in a series of experiments in which the procedure was similar to that described above, except that 40 c.c. of the appropriate buffer solution replaced the aldehyde solution.

Table I shows the observed rotations at different p_H values of 0·005M-d-phenylalanine alone and at equilibrium with 1 mol. of 2 : 3- and 3 : 4-dimethoxybenzaldehydes.

TABLE I.

[a = observed rotation; T = time (mins.) required to reach equilibrium; I = increase in a due to condensation.]

p_H.	Phenylalanine alone.	2 : 3-Dimethoxybenzaldehyde.			3 : 4-Dimethoxybenzaldehyde.		
		a.	T.	I.	a.	T.	I.
7	+ 0·14°	—	—	—	—	—	—
8	0·12	+ 0·17°	5	0·05°	+ 0·12°	—	0
9	0·09	0·20	6	0·11	0·13	10	0·04°
9·3	0·07	0·25	9	0·18	0·13	>45	0·06
9·6	0·04	0·28	14	0·24	0·12	>27	0·08
10·0	0·03	—	—	—	—	—	—

Proof of the Reversibility of the Condensation of Dimethoxybenzaldehydes with Phenylalanine.— (i) *With 1 mol. of aldehyde.* A mixture of d-phenylalanine (0·25 millimol.), 2 : 5- or 3 : 4-dimethoxybenzaldehyde (0·25 millimol.), and sodium hydroxide (0·25 millimol.) in 50% ethyl alcohol (5·0 c.c.) was shaken until clear and then allowed to attain equilibrium as shown by a constant rotation; the portion not in the polarimeter tube was exposed simultaneously to the light of the mercury arc, in case this catalysed the formation of arylidenediarylhydroxyethylamine (cf. Erlenmeyer, *Annalen*, 1899, 307, 118).

The whole solution was then brought to about p_H 4 (B.D.H. capillator) by the addition of 4 drops of glacial acetic acid, added, as in all these experiments, from a standard-drop pipette so as to ensure constant conditions. The observed rotation of the acidified solution was + 0·20°, (l = 0·5), whereas in a control experiment without aldehyde the rotation of d-phenylalanine alone was + 0·19°.

(ii) *With 3 mols. of aldehyde.* Control 1. Glacial acetic acid (4 drops) was added to a solution of d-phenylalanine (41·25 mg.; 0·25 millimol.) and sodium hydroxide (0·25 millimol.) in 50% ethyl alcohol (5·0 c.c.). The p_H of the solution was about 4, and the observed rotation was + 0·40° (l = 1).

Control 2. Glacial acetic acid (4 drops) and then sodium hydroxide (0·25 millimol.) in 50% alcohol were added in that order to a mixture of d-phenylalanine (0·25 millimol.) and one of the three dimethoxybenzaldehydes (0·75 millimol.) in 50% alcohol (3·75 c.c.). When the solid had completely dissolved, the solution was diluted to 5·0 c.c. with 50% alcohol. The observed rotation was + 0·58° (l = 1). Hence the presence of 124·5 mg. of aldehyde raised the rotation by + 0·18°.

The actual experiment was carried out as described above, except that the order of addition of the sodium hydroxide and acetic acid was reversed, and time was allowed for the attainment of equilibrium before acidification. The observed rotations for the acidified solutions were: 2 : 5-dimethoxybenzaldehyde, + 0·57°; 2 : 3- and 3 : 4-dimethoxybenzaldehydes, + 0·58°.

Identification of recovered phenylalanine. (i) The acidified control solution No. 2 or experimental solutions were mixed with 2N-hydrochloric acid (0·5 c.c.) and water (15 c.c.). The mixture was extracted with ether in a continuous-extraction apparatus for 2 hours to remove the

aldehyde, and the residual aqueous layer was mixed with 2N-sodium hydroxide (0·6 c.c.), *p*-toluenesulphonyl chloride (200 mg.), and some ether, and shaken mechanically whilst being kept just alkaline by the addition of successive portions of 0·1 c.c. of 2N-sodium hydroxide until it remained alkaline for more than 1 hour. The alkaline solution was concentrated to small volume under reduced pressure, treated with a little charcoal, filtered, and acidified with excess of hydrochloric acid; its volume was then adjusted to 16 c.c., if necessary, by addition of water. The toluenesulphonyl derivative crystallised immediately, and after remaining at 0° for some time, was collected, washed with water (2 c.c.), and dried in a vacuum desiccator. The derivatives from the control experiment and from those with 2 : 5- and with 3 : 4-dimethoxy-benzaldehydes weighed respectively 70·7, 70·2, and 69·6 mg., having crude m. p.'s 151°, 150°, and 149°, and raised by recrystallisation from 50% ethyl alcohol to 164°, 163°, and 163° (all corr.) respectively, in each case with previous softening; the theoretical yield is 79·7 mg., and Fischer and Lipschitz (*Ber.*, 1915, **48**, 369) give m.p. 164—165° (corr.) with previous softening.

(ii) Solutions were prepared from phenylalanine (61·9 mg.; 1 mol.) in water (3·0 c c.), sodium hydroxide (1 mol.) in 50% alcohol (1·5 c.c.), and 2 : 5-dimethoxybenzaldehyde (3 mols.) in alcohol (3 c.c.) or, in the control experiment, alcohol (3 c.c.) alone. When the mixture containing the aldehyde had come to equilibrium, 2N-hydrochloric acid (0·5 c.c.) was added to each mixture, and they were extracted three times with ether. 2N-Sodium hydroxide (0·6 c.c.) and α-naphthyl *iso*cyanate (0·74 c.c.) were then added, and the solutions were kept alkaline and shaken for 30 minutes, and filtered. The filtrates were cloudy, and after several days naphthylamine had separated from both solutions. This was removed, and the clear filtrates were acidified. The carbamido-acid separated from both solutions in a gelatinous condition, but was ultimately collected, washed with water, and dried over phosphoric oxide. The yields were 82·6 mg. from the experimental and 79·6 mg. from the control solutions (theory, 125·2 mg.). When recrystallised once from aqueous alcohol, both specimens weighed 65—70 mg , and both melted at 152° (corr.), with previous softening. α-2-Naphthylcarbamido-β-phenylpropionic acid melts at 155° after softening at 150° (Neuberg and Rosenberg, *Biochem. Z.*, 1907, **5**, 456).

Identification of recovered 2 : 5-dimethoxybenzaldehyde. 2 : 5-Dimethoxybenzaldehyde (186·7 mg.; 3 mols.) in alcohol (3 c.c.) was added to phenylalanine (61·9 mg.; 1 mol.) in water (3 c.c.) and sodium hydroxide (1 mol.) in 50% alcohol (1·5 c.c.). This solution was allowed to attain equilibrium, and simultaneously a control solution was prepared in which the amino-acid solution was replaced by water (3 c.c.). Both solutions were acidified with 2N-hydrochloric acid (0·2 c.c.), and extracted with ether in a continuous-extraction apparatus. The extracts were concentrated, and the residues dissolved in alcohol (15 c.c.) and added to 2 : 4-dinitro-phenylhydrazine (0·35 g.) in a mixture of concentrated sulphuric acid (0·7 c.c.) and alcohol (5 c.c.). After standing over-night at 0°, the 2 : 4-dinitrophenylhydrazones were collected, washed with alcoholic sulphuric acid, then with alcohol, and dried. The yields of crude product were 98% and 97% from the experiment and the control respectively, and when crystallised from xylene the two products formed orange prisms, m.p. 199—201°, undepressed on admixture.

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49. *Tribromogold.*

By Abraham Burawoy and Charles S. Gibson.

There is no evidence for the existence of the tervalent gold ion (Au+++),* and tervalent gold can exist as part of a tervalent kation only when suitably co-ordinated in such a compound as diethylenediaminogold tribromide, [Au en$_2$]Br$_3$ (Gibson and Colles, *J.*, 1931, 2410).

The organic compounds of gold containing tervalent gold all contain 4-covalent gold and it seemed desirable to determine whether there is any evidence for assigning a constitution to tribromogold analogous to that of organic compounds of tervalent gold which are non-electrolytes. Obviously, such evidence may be obtained from molecular-weight

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* For this reason and as a consequence of the present investigation as well as of the work of other authors, the gold trihalides are more systematically named, for example, as trichlorogold and tribromogold.

determinations of tribromogold prepared as described by Gibson and Colles (*loc. cit.*). Fischer has found the molecular formula of " auric chloride " vapour between 150° and 260° to be Au_2Cl_6 (*Z. anorg. Chem.*, 1929, **184**, 333).

Although tribromogold is stable in bromoform and in bromine, its solubility in these liquids at their melting points is far too small to permit of molecular-weight determinations by the cryoscopic method. Even at the boiling point, the solubility of tribromogold in bromine (in which its dissociation must be negligible) is still small, but this seems to be the only solvent in which direct determinations of the molecular weight are possible.

The method employed was that of Beckmann (*Z. physikal. Chem.*, 1902, **40**, 129; 1903, **44**, 164), in which the solution is heated by the vapour of the solvent boiling in an outer jacket, allowing, for a given weight of solute, four determinations of the molecular weight to be made with 7·4, 10·8, 14·2, and 17·5 c.c. of solution at the boiling point. The apparatus was constructed entirely of glass and a Beckmann micro-thermometer made to suit the apparatus was used, the bulb being always completely immersed in the solution. The molecular elevation of the boiling point of bromine was assumed to be 52 (Beckmann, *Z. physikal. Chem.*, 1900, **46**, 853), and the density of bromine at the boiling point 2·948. The following are two typical series of results :

(1) With 0·2100 g. : Δ 0·048°, 0·033°, 0·035°, 0·020°; *M*, 1043, 1039, 1058, 745.
(2) With 0·2569 g. : Δ 0·062°, 0·047°, 0·045°, 0·032°; *M*, 987, 892, 809, 709.

The average value for the molecular weight of tribromogold thus found is approximately 910 [Calc. for $(AuBr_3)_2$: *M*, 874].

The experimental error in any one determination is large. In the two series of results recorded, the highest elevation of the boiling point observed was 0·062° and the lowest 0·020° and there may be an error as high as 0·005° in the actual observation. In spite of this, the experiments show that the molecular weight of tribromogold is twice that demanded by its empirical formula. This implies that the constitution of the compound may be expressed by the

formula $\begin{smallmatrix} Br \\ Br \end{smallmatrix} Au \begin{smallmatrix} Br \\ Br \end{smallmatrix} Au \begin{smallmatrix} Br \\ Br \end{smallmatrix}$. Tribromogold thus has a constitution analogous to that of the organic compounds of tervalent gold in which the gold atoms are 4-covalent and which are non-electrolytes.*

No evidence of the formation of an ethoxy-derivative of gold (or of a pyridine derivative of such a compound) has been obtained by allowing a strongly cooled suspension of tribromogold in ether to react with either 2 or 3 mols. of potassium ethoxide in alcoholic solution. In the former case, potassium bromide and a small quantity of gold having been removed, the brownish red filtrate was treated with pyridine and the greyish precipitate produced was recrystallised from pyridine below 40° or, better, by addition of ether to the pyridine solution; the product separated in colourless crystals of *monopyridinomonobromogold*, Py→Au–Br, decomposing above 120° or on standing or on heating with solvents, including pyridine (Found : Au, 54·7. C_5H_5NBrAu requires Au, 55·3%). In the latter case, the tribromogold was quantitatively reduced to gold, and potassium bromide (3 mols.) obtained.

When pyridinotribromogold (Gibson and Colles, *loc. cit.*) reacted under similar conditions with potassium ethoxide (2 mols.), the red gold compound was converted into a yellowish-grey mixture of potassium bromide and monopyridinomonobromogold. The latter was extracted with pyridine, the pyridine solution evaporated at the ordinary temperature over sulphuric acid, and the residue purified by precipitation from pyridine solution with ether. It was monopyridinomonobromogold, identical with that previously obtained (Found : Au, 54·7%).

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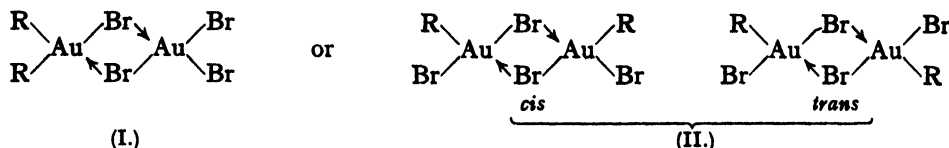
* The magnetic susceptibility of tribromogold, kindly determined by Professor S. Sugden, F.R.S. (J., 1932, 161), is $\chi = -0.23 \times 10^{-6}$ e.m.u. at 19°, confirming the diamagnetic nature of the compound.

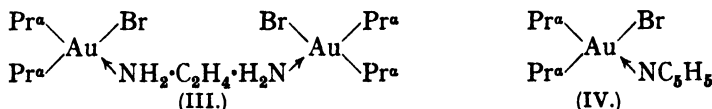**50. *The Organic Compounds of Gold. Part IV. n-Propyl Compounds.***

By Abraham Burawoy and Charles S. Gibson.

THE chemical properties of monoethyldibromogold (discussed in Part III; Burawoy and Gibson, J., 1934, 860) and its molecular weight in freezing bromoform indicate that the constitution of this type of compound can be either (I) or (II) (R = Et).

$$\underset{\text{(I.)}}{\overset{R}{\underset{R}{>}}Au\overset{Br}{\underset{Br}{<}}\overset{Br}{\underset{Br}{>}}Au\overset{Br}{\underset{Br}{<}}} \qquad or \qquad \underset{\underset{cis}{\underbrace{\hphantom{xxxxxxxxxx}}}}{\overset{R}{\underset{Br}{>}}Au\overset{Br}{\underset{Br}{<}}\overset{R}{\underset{Br}{>}}Au\overset{R}{\underset{Br}{<}}} \qquad \underset{\underset{trans}{\underbrace{\hphantom{xxxxxxxxx}}}}{\overset{R}{\underset{Br}{>}}Au\overset{Br}{\underset{Br}{<}}\overset{Br}{\underset{Br}{>}}Au\overset{Br}{\underset{R}{<}}}$$

$$\text{(II.)}$$

Whatever be the configuration of the atoms and groups attached to the 4-covalent gold atoms, the *cis*- and the *trans*-forms (II) are theoretically possible. The spontaneous and quantitative decomposition of monoethyldibromogold into ethyl bromide and aurous bromide is easily explained on that constitutional formula; on the other hand, its chemical properties, its formation from diethylmonobromogold and tribromogold (auric bromide), and its colour are more in keeping with constitution (I). It has too low a solubility in carbon tetrachloride (it is decomposed in benzene) to permit of a measurement of its dipole moment which would throw additional light on its constitution; so, to complete the investigation of this type of gold compound, a detailed study has been made of its homologue, *mono*-n-*propyldibromogold*.

Di-n-propylmonobromogold (Kharasch and Isbell, *J. Amer. Chem. Soc.*, 1931, **53**, 2701) was obtained from pyridinotrichlorogold and n-propylmagnesium bromide and isolated in the form of *monoethylenediaminotetra*-n-*propyldibromodigold* (III), a colourless crystalline compound which is a non-electrolyte. No corresponding derivative of diethylmonobromo-

$$\underset{\text{(III.)}}{\overset{Pr^{a}}{\underset{Pr^{a}}{>}}Au\overset{Br}{\underset{NH_{2}\cdot C_{2}H_{4}\cdot H_{2}N}{<}}\overset{Br}{\underset{}{>}}Au\overset{Pr^{a}}{\underset{Pr^{a}}{<}}} \qquad\qquad \underset{\text{(IV.)}}{\overset{Pr^{a}}{\underset{Pr^{a}}{>}}Au\overset{Br}{\underset{NC_{5}H_{5}}{<}}}$$

gold has been obtained, but the compound is analogous to the monoammino- and mono-pyridino-diethylmonobromogold compounds of Gibson and Simonsen (*J.*, 1930, 2531) and also to the *monopyridinodi*-n-*propylmonobromogold* (IV) now to be described.

Monoethylenediaminotetra-n-propyldibromodigold (III) is insoluble in water and ligroin, soluble in alcohol, chloroform, and nitrobenzene, and sparingly soluble in benzene, bromoform, and *cyclo*hexane. In a melting-point tube, it has m. p. 110—111°, gas being evolved; the product (often slightly discoloured) then solidifies and decomposes at about 140°, frequently with explosion. The action of heat on compound (III) is further described below.

A solution of (III) in chloroform after a while deposits colourless needles of ethyl-enediaminodi-n-propylgold bromide (Gibson and Colles, *J.*, 1931, 2413), more rapidly when concentrated than when dilute; the formation takes place as follows,

$$2Pr^{a}{}_{2}AuBr\cdot en\cdot AuBrPr^{a}{}_{2} \rightleftharpoons 2[Pr^{a}{}_{2}Au\ en]Br + Pr^{a}{}_{2}AuBr\cdot AuBrPr^{a}{}_{2}$$

the salt being insoluble and di-n-propylmonobromogold (an oil at the ordinary temperature) being readily soluble in chloroform. Owing to this behaviour, the purification of (III) by solution in chloroform and addition of ligroin until crystallisation commences must be carried out in not too concentrated solution and as rapidly as possible. A similar decomposition takes place when (III) is repeatedly washed with small quantities of water; the aqueous filtrate contains a small but quite recognisable amount of ethylenediaminodi-n-propylgold bromide.

It has not been possible to control the decomposition of pure monoethylenediaminotetra-n-propyldibromodigold (III) in quantity by heat, which may proceed explosively even

below 100°; but the action of heat on solutions of the compound can be investigated conveniently. When clear solutions of (III) in benzene, cyclohexane, and chloroform are heated on the water-bath, colourless needles separate (those from the first two solutions, when dilute, are generally discoloured owing to slight reduction of the gold compound). The product, which is best obtained by gently boiling the chloroform solution for a few minutes, and is insoluble in water and ligroin, sparingly soluble in chloroform, and easily soluble in alcohol, is *monoethylenediaminodi-n-propyldibromodigold* (V), in which one gold atom is univalent and 2-covalent and the other is tervalent and, as in all other cases of tervalent gold compounds, 4-covalent. This compound decomposes at about 140° with explosive violence and it must be identical with the product formed when gas is evolved from (III) in a melting-point tube :

$$Pr^a{}_2AuBr \cdot en \cdot AuBrPr^a{}_2 \longrightarrow \begin{matrix} Pr^a \\ Pr^a \end{matrix} Au \begin{matrix} Br \\ NH_2 \cdot C_2H_4 \cdot H_2N \end{matrix} \begin{matrix} Br \\ \end{matrix} Au + 2Pr^a$$

(III.)   (V.)
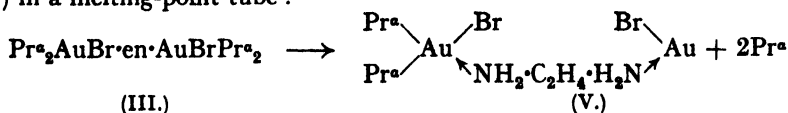
Whether free *n*-propyl radicals are actually evolved during the decomposition of (III) has not been determined, but their production would seem to be the correct explanation of the action of heat on monoethylenediaminotetra-*n*-propyldibromodigold. The further decomposition of monoethylenediaminodi-*n*-propyldibromodigold has not been investigated.

When compound (III) is shaken with carbon tetrachloride and dilute hydrobromic acid, it yields a carbon tetrachloride solution of di-*n*-propylmonobromogold. This solution, of known concentration (1 mol.), is mixed with a carbon tetrachloride solution containing rather less than the calculated quantity of bromine (2 mols.) and, after some hours, allowed to evaporate to dryness. The crystalline residue after purification as described later, is *mono-n-propyldibromogold*, which is obtained in dark red, doubly refracting prisms. Its molecular weight in freezing bromoform indicates the formula $[Pr^aAuBr_2]_2$; unlike the corresponding ethyl compound, it has a melting point (54°) and it is much more highly soluble in such solvents as chloroform, bromoform, and carbon tetrachloride. In its chemical properties it is exactly analogous to the ethyl compound. Although it is more stable than its ethyl analogue, it decomposes quantitatively, very slowly at the ordinary temperature and rapidly above its melting point, into *n*-propyl bromide and aurous bromide :

$$[Pr^aAuBr_2]_2 \longrightarrow 2Pr^aBr + 2AuBr$$
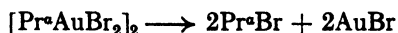
When it is shaken with aqueous potassium bromide, a solution of potassium bromoaurate is obtained and di-*n*-propylmonobromogold separates as a colourless oil. Mono-*n*-propyldibromogold is decomposed by solvents which are easily brominated or oxidised, yielding solutions of di-*n*-propylmonobromogold and precipitates of aurous bromide, which may be partly reduced to gold. Like its ethyl analogue, it does not form derivatives of itself : when solutions of the compound and pure pyridine in carbon tetrachloride are mixed, monopyridinodi-*n*-propylmonobromogold (see above), soluble in carbon tetrachloride, and a scarlet precipitate of pyridinotribromogold are obtained, the solution becoming practically colourless; theoretical quantities of both compounds are obtained according to the equation

$$[Pr^aAuBr_2]_2 + 2Py \longrightarrow Pr^a{}_2AuBrPy + PyAuBr_3$$
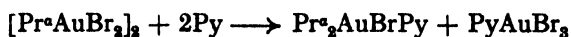
The dipole moments of organic gold compounds have not been previously measured, and that of diethylmonobromogold was first investigated : * a zero dipole moment would confirm the symmetrical constitution already assigned to the compound (J., 1930, 2531). The dipole moment was measured in benzene solution at 25°, the dielectric constant being determined by Sugden's method (J., 1933, 768) with a silver condenser. The results are tabulated below (f_2 = molar fraction of the solute, d, e, and n = density, dielectric constant, and refractive index of the solution, $p_{1, 2}$ = specific polarisation,

* The authors are indebted to Professor S. Sugden, F.R.S., for kindly affording them facilities for carrying out this determination.

P_2 = total polarisation of the solute, P_E = the electron polarisation calculated from the refractive index, and $P_\mu = P_2 - P_E$ when $P_E = 102.2$) :

f_2.	$d^{25°}$.	$\epsilon^{25°}$.	$p_{1, 2}$.	P_2.	$n^{25.5°}_{5760}$.	P_E.	P_μ.
—	0·8732	2·2730	0·3412	—	1·4992	—	—
0·001849	0·8815	2·2745	0·3383	106·7	—	—	4·5
0·004199	0·8949	2·2855	0·3354	118·4	1·5021	102·1	16·2
0·006893	0·9087	2·2960	0·3321	120·8	—	—	18·6
0·010140	0·9225	—	—	—	1·5049	102·2	—

Regarding the accuracy of the results, (1) the infra-red term is neglected, (2) since the compound has a high molecular weight, comparatively dilute solutions are used, and (3) diethylmonobromogold is not completely stable in benzene, in which it is conveniently soluble, and though during the determinations very little decomposition takes place, such solutions show considerable decomposition after two days. The actual values consequently may not be appreciably different from zero and, in any case, the actual dipole moment is certainly less than 1.0×10^{-18} e.s.u. This is in agreement with the symmetrical constitution,

$$\underset{R}{\overset{R}{\diagdown}}Au\underset{Br}{\overset{Br}{\diagdown}}Au\underset{R}{\overset{R}{\diagdown}}$$

, for the dialkyl compounds. The simple constitution, AuR_2Br, is excluded (as, indeed, it is also excluded by the known molecular weight in the case of the diethyl compound); it would also require a comparatively high dipole moment, and the polarisation calculated with half the value of the true molecular weight would be still lower than the above, confirming a zero dipole moment.

Owing to the immediate reaction between mono-n-propyldibromogold in carbon tetrachloride solution and silver, it was impossible to use a silver condenser for the determination of the dipole moment of this compound. This has been carried out on the freshly prepared substance in carbon tetrachloride solution by Mr. G. C. Hampson, M.A., in the Dyson Perrins Laboratory of the University of Oxford, using a platinum condenser at 25°.* The results are :

	f_2.	$d^{25°}$.	$\epsilon^{25°}$.	P_2	μ (assuming a value of $P_E = 108$ c c , calcd. from $[Et_2AuBr]_2$)
	0·0	1·5853	2·2272	—	—
A	0·008091	1·6200	2·5407	664	5.2×10^{-18} e s u.
B	0·004617	1·6038	2·3906	634	5·0 ,,
C	0·006872	1·6152	2·5337	752	5·6 ,,
D	0·003463	1·6009	2·3914	813	5·8 ,,

Owing to the deep violet colour of the solutions the refractive index could not be determined, it was calculated from that of diethylmonobromogold.

In these determinations there are slight inconsistencies. Determination (B) (lower concentration) indicates a lower dipole moment than (A), both carried out on the same day; whereas determinations (C) and (D) give results in the right order. Platinum has a very slight action on these gold compounds and some slight action was noticed during the determinations. The solutions themselves were fairly stable, though the dielectric constant fell slightly when they were left in the condenser for some time. The deposit (very small) could be removed and the replaceable capacity of the condenser did not change during the measurements, as was shown by the agreement between the calibrations for air and pure carbon tetrachloride before and after the experiments. It is possible that less reaction (which was small in any case) took place during the second determinations (C and D) than during the first two and hence the greater consistency of the former. The determinations, however, show clearly that the order of magnitude of the dipole moment is not lower than 5×10^{-18} and may be as high as 6×10^{-18} e.s.u. Such a high dipole moment indicates an unsymmetrical structure for mono-n-propyldibromogold in particular and analogous compounds in general. The possible unsymmetrical constitutions are (I) and the *cis*-form of (II). The compound as obtained in the many preparations is always homogeneous

* The authors are greatly indebted to Mr. Hampson for his willing co-operation and for the great care with which the determinations were made. The experience gained in this work shows that in the comprehensive study of the dipole moments of organic gold compounds an all-gold condenser should be used.

and it is unlikely that the *cis*-form is more stable than the *trans*-form of such a compound. The compound cannot be the *trans*-modification, which would have a low or zero dipole moment. The evidence, therefore, from the measurement of the dipole moment is in favour of constitution (I), which, as indicated above, is in keeping with the chemical and general physical properties of the substance.

Since a number of diverse types of organic gold compounds have become or are becoming available, it is to be hoped that a detailed investigation of the dipole moments of representative types will be undertaken, and a discussion of the origin of the high dipole moment of the monoalkyldibromogold compounds may be postponed until a larger number of gold compounds has been examined. In the meantime, the high dipole moment of mono-*n*-propyldibromogold may be compared with those of the triethylstannic chloride ($3·44 \times 10^{-18}$) and diethylstannic dichloride ($3·85 \times 10^{-18}$) recently investigated by Spaght, Hein, and Pauling (*Physikal. Z.*, 1933, **34**, 212).

<center>EXPERIMENTAL.</center>

*Monoethylenediaminotetra-*n*-propyldibromodigold* (III).—To a mechanically stirred suspension of pyridinotrichlorogold (40 g., prepared as described by Burawoy and Gibson, J., 1934, 860) in dry pyridine (300 c.c.), a filtered solution of *n*-propylmagnesium bromide [prepared from magnesium (5·6 g.), *n*-propyl bromide (28·4 g., 2·2 mols.), and ether (60 c.c.)] is added during 3 minutes while the mixture is cooled in a freezing mixture. After a further 10 minutes' stirring, water at 0° (100 c.c.) is added, followed by ligroin (b. p. 40—60°, 300 c.c.) and hydrobromic acid (*d* 1·49, 450 c.c.) at such a rate that the temperature does not rise above 30—40°. The mixture is stirred for a further 30 minutes and then filtered from precipitated gold and any unchanged pyridinotrichlorogold. The ligroin solution is separated, washed with water, and shaken with ethylenediamine until no further colourless precipitate of ethylenediaminodi-*n*-propylgold bromide, [Pr_2Au en]Br (Gibson and Colles, *loc. cit.*), is produced. This precipitate is removed by extraction with water and the treatment of the ligroin solution with ethylenediamine is repeated until no further precipitate is formed. To the filtered aqueous solution, hydrobromic acid is carefully added until no further colourless precipitate is produced; it is important to avoid an excess of the acid. The compound is separated, washed with a small quantity of water and then with ligroin, and dried over phosphoric oxide. It may be purified by adding ligroin to a filtered chloroform solution until crystallisation takes place, the operation being carried out rapidly; yield, 6·4 g. or 15·6% of the theoretical amount, varying in different preparations from 12 to 21%. By using pyridinotribromogold (37 g.) and proceeding in a similar manner, the same compound (4 g.; yield, 14·5%) is obtained.

*Monoethylenediaminotetra-*n*-propyldibromodigold* is a colourless crystalline compound; its properties and behaviour on being heated are described on p. 219. The determination of the gold content is somewhat difficult, since the compound explodes not only when heated in bulk but also on treatment with bromine and with sulphuric acid. The bromine content was determined by treatment with sodium methoxide in methyl alcohol on the water-bath for 1 hour and subsequent titration with silver nitrate and potassium thiocyanate. The nitrogen was determined by microanalysis, and the molecular weight by the cryoscopic method [Found : N, 3·4; Br, 20·4, 20·5; Au, 49·6; *M*, 791, 753 (nitrobenzene). $C_{14}H_{36}N_2Br_2Au_2$ requires N, 3·6; Br, 20·35; Au, 50·1%; *M*, 786·5].

Ethylenediaminodi-*n*-propylgold bromide produced from (III) in the manner described above was identical with an authentic specimen (Found : Au, 46·8; calc., 46·6%).

*Monoethylenediaminodi-*n*-propyldibromodigold* (V) is produced by the action of heat on (III). Its preparation and properties have been described above (Found : Br, 23·1, 23·0; Au, 56·6, 56·4. $C_8H_{22}N_2Br_2Au_2$ requires Br, 22·8; Au, 56·3%).

*Mono-*n*-propyldibromogold* (as I, R = C_3H_7[a]).—Monoethylenediaminotetra-*n*-propyldibromodigold (11·6 g.) is shaken with an excess of hydrobromic acid, the liquid di-*n*-propylmonobromogold being liberated. This is extracted with a small quantity of carbon tetrachloride, the solution washed with water, dried with anhydrous sodium sulphate, and evaporated at the ordinary temperature under reduced pressure to about 15 c.c. To this filtered solution, bromine in carbon tetrachloride (1·63*N*, 34·0 c.c.; theo. for 2 mols., assuming the above constitution, 36·3 c.c.) is added, and the mixture kept in a glass-stoppered vessel for 24 hours. The deep red solution is allowed to evaporate spontaneously and the crystalline residue is recrystallised from carbon tetrachloride by obtaining a solution at a temperature not higher than 40°, filtering it

through fine sintered glass, and cooling it in a freezing mixture (yield, 6 g., apart from about 1 g. obtained from the mother-liquor). The compound crystallises in dark red, doubly refracting prisms having a purple metallic lustre. It has m. p. 54°, above which it begins to decompose. Its molecular weight is determined in freezing bromoform (Found : Br, 39·95; Au, 48·8, 49·4; M, 777·5, 809. $C_6H_{14}Br_2Au_2$ requires Br, 39·95; Au, 49·3%; M, 800·2).

The greater stability of *mono*-n-*propyldibromogold* over the corresponding ethyl derivative is shown by the fact that a specimen kept for a month at 18—22° suffered a loss in weight of only 1·8%, but a slight rise in temperature causes a rapid increase in the rate of decomposition (compare Burawoy and Gibson, *loc. cit.*). When the compound is heated at 80—85°, its decomposition into n-propyl bromide and aurous bromide is complete in 30 minutes (Found : loss, 30·5. $[Pr^aBr_2Au]_2$ requires for loss of $2Pr^aBr$, 30·7%). The yellowish-green residue is pure aurous bromide (Found : Au, 71·2; calc., 71·1%).

To mono-n-propyldibromogold (2·62 g.) in carbon tetrachloride (20 c.c.), pyridine (0·52 g.; 2 mols.) is added. The violet colour is immediately destroyed and a red compound is precipitated. The latter, after separation and washing with carbon tetrachloride, is identified by comparison with an authentic specimen and by analysis as pyridinotribromogold (Found : Au, 38·2; calc., 38·2%). The slightly reddish filtrate from the pyridinotribromogold (obtained in almost quantitative amount) is evaporated, and the residue recrystallised from ligroin. It is obtained in colourless needles, m. p. 61—62°, soluble in benzene, chloroform, and carbon tetrachloride and almost insoluble in ligroin at the ordinary temperature. The same compound is prepared by allowing di-n-propylmonobromogold to react with pyridine in ligroin. It is *pyridinodi-n-propylmonobromogold* (IV), $PyPr^a_2AuBr$ (Found : Au, 44·7, 44·6. $C_{11}H_{19}NBrAu$ requires Au, 44·6%).

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51. *Autoxidation Processes. Part VIII.* Steric Hindrance in Oxidation and Racemisation of α-Ketols.*

By Arnold Weissberger.

It has been shown in previous papers of this series that a relation exists between the rates of autoxidation, oxidation with Fehling solution, and racemisation of α-ketols $R\cdot CH(OH)\cdot CO\cdot R'$ in alkaline solution, and the electrolytic dissociation constants of the carboxylic acids $R\cdot CO_2H$ and $R'\cdot CO_2H$. Table I shows for a series of α-ketols (one aliphatic, and the others benzoin and p-substituted benzoins) the autoxidation velocities k at 10° and at 20° in 79% ethyl-alcoholic solution in the presence of 0·05N-potassium hydroxide, the ketol concentration being 0·0057M. Col. 4 gives the values of the empirical relation between $k_{20°}$ and the dissociation constants (K and K') of the carboxylic acids, $k_{20°}/(KK')^{1·8}$ =const., the constancy being reasonably good. Of m-substituted benzoins, hitherto only piperonyloin and mm'-dimethoxybenzoin had been investigated. The ratio for the former, a p-substituted compound also, agrees with the average value for the other ketols in Table I ; that for the latter (Table II) is rather lower. For the m-substituted benzoins in general there are three possibilities : they might give a value of the ratio identical with that of the p-compounds, or an average value somewhat different, or thirdly, they might obey no simple relation at all. The last had been shown to be the case with the o-substituted benzoins, and this failure was attributed to steric hindrance. To examine this interpretation is the main purpose of the present paper.

It was found that these steric effects played no part whatever in the m-compounds,

TABLE I.

Benzoin.	$10^3k_{10°}.$	$10^3k_{20°}.$ $10^{10} \times KK'.‡$	$10^{-13}k_{20°}/(KK')^{1.8}.$	$10^6(x-x').§$
1. (Butyroin)	0·93	2·1	2·25	49	—
2. *p'-Dimethylamino-	2·6	9·7	6·2	36	—
3. p'-Chloro-p-dimethylamino-	11·1	32	8·74	65	—
4. pp'-Diethoxy-	15·6	49	—	74 †	—
5. pp'-Dimethoxy-	17·4	61	10·2	93	8·1
6. pp'-Diisopropyl-	38·4	98	27·04	26	—
7. pp'-Dimethyl-	41·7	101	18·7	52	9·0
8. 3 : 4 : 3' : 4'-Di(methylenedioxy)-	42·4	108	20·2	48	9·8
9. p'-Methyl-	54	140	28·6	34	10
10. p-Methyl-	66	180	28·6	44	10·1
11. Benzoin	97	270	43·6	30	12·1
12. p'-Chloro-	258	674	61·4	41	21·3
13. p-Chloro-	330	770	61·4	47	22·1
14. pp'-Dichloro-	668	~1500	86·5	49	37·4

* The dash marks the ring adjacent to the carbonyl group.
† Calculated from K for p-methoxybenzoic acid.
‡ From Landolt–Börnstein–Roth and International Critical Tables.
§ See Part IX.

TABLE II.

Benzoin.	$10^3k_{10°}.$	$10^3k_{20°}.$	$10^{10} \times KK'.$	$10^{-13}k_{20°}/(KK')^{1.8}.$	$10^{-13}k_{10°}/(KK')^{1.8}.$	$10^6(x-x').$
15. mm'-Dimethoxy-	108	300	79·4	12	3·9	13·7
16. mm'-Diethoxy-	115	290	—	11	4·3	—
17. mm'-Dichloro-	980	—	240·3	—	5·1	59·6

as shown in Table II, but are confined to the *o*-derivatives. The ratios with the $k_{20°}$ values are given only for the first two compounds, since *mm'*-dichlorobenzoin is too reactive to be investigated at 20°. For this substance, therefore, the ratio with the $k_{10°}$ value is given, together with the corresponding ratios for the other two substances. The value of the ratio for the three *m*-derivatives is constant, and is about one-third of that for the compounds in Table I. This difference will be discussed in a subsequent paper. The three derivatives with methoxyl, ethoxyl, and chlorine, however, all behave in the same way; the *autoxidation rates of the meta-substituted benzoins are linked without individual deviations to the dissociation constants of the carboxylic acids*, just as in the case of the para-substituted compounds.

If, however, the same substituents are introduced into the *o*-position, they cause large individual deviations from the relation in question, as appears from Table III. The values in col. 4 for the benzoins with ortho-substituents in *both* rings (Table IIIa) decrease as one goes from methyl through methoxyl to ethoxyl, *i.e.*, they fall with increasing volume of the substituents, as would be expected for a steric effect. The decrease for the dichloro-compound is so large as to require special discussion (see Part IX, succeeding paper). Table III*b*, which concerns the derivatives with only one substituent in the *o*-position, shows the same regularity, and further, shows that the *o*-effect of the substituent is larger if it is introduced into the ring next to the hydroxyl group than into the other nucleus.

TABLE IIIa.

Benzoin.	$10^3k_{10°}.$	$10^3k_{20°}.$	$10^{10} \times KK'.$	$10^{-13}k_{20°}/(KK')^{1.8}.$	$10^{-13}k_{10°}/(KK')^{1.8}.$	$10^6(x-x').$
18. oo'-Dimethyl-	72	200	148·8	2·5	—	15·8
19. oo'-Dimethoxy-	12·4	34	67·2	1·7	—	7·9
20. oo'-Diethoxy-	3·6	9·8	74·0	0·42	—	7·7
21. oo'-Dichloro-	510	1250	16900	0·0051	—	54·6

TABLE IIIb.

22. o'-Methyl-	360	880	80·5	33	—	21·9
23. o-Methyl-	170	460	80·5	17	—	20·0
24. o'-Ethoxy-	88	218	56·8	15	—	9·8
25. o-Ethoxy-	44	114	56·8	7·9	—	8·3
26. o-Chloro-	295	735	858·0	0·39	—	22·9

These facts, *viz.*, that the relation between the dissociation constants and the rates of reaction holds in the para- and the meta- but not in the ortho-substituted benzoins,

and that the deviations in the last series increase with the volume of the substituents, provide conclusive evidence that these deviations are caused by steric hindrance.

EXPERIMENTAL.

Measurements were made as described in the previous papers of this series.

Materials.—mm'-*Dichlorobenzoin.* A solution of potassium cyanide (0·5 g. in water, 3 c.c.) was added to *m*-chlorobenzaldehyde (10 g.) in ethyl alcohol (20 c.c.), heated at 60° for 5 hours (air being excluded), poured into ice-water which was kept *acid* by hydrochloric acid, shaken with ether, and the ethereal layer steam-distilled. The residue was dissolved in ether, dried (sodium sulphate), the ether removed, and the residue dissolved in a little ligroin. A part of this solution, on being cooled in solid carbon dioxide–ether, gave crystals; the rest, when seeded with these, crystallised at 0°. After repeated crystallisations from ligroin, 2·2 g. (22%) of a colourless product were obtained, m. p. 76° (sintering at 69°). The substance solidifying from the melt remelted sharply at 75—76°, and after seeding with this the main bulk also gave crystals of m. p. 75—76°. Investigation under the hot-stage microscope confirmed that the substance is polymorphous (Found : C, 59·9; H, 3·4; Cl, 24·9. Calc. : C, 59·8; H, 3·6; Cl, 25·2%). Klimont (Diss., Heidelberg, 1891) describes the compound as light yellow, m. p. 65—67°.

o-Methylbenzoylphenylcarbinol (o'-*Methylbenzoin*). We had previously prepared this compound (*Annalen*, 1931, **478**, 126) according to the method of McKenzie, Martin, and Rule (J., 1914, **105**, 1586) and obtained a product, m. p. 108—109°, which we believed to be the right substance as it had the properties given in the literature. When, however, we used *o*-bromotoluene prepared from purified *o*-toluidine, instead of Kahlbaum's material, we obtained a ketol of m. p. 74—75°, having the autoxidation velocities given in Table III*b*. This compound is the true *o*-methylbenzoylphenylcarbinol, whilst the compound of higher m. p. is the *p*-derivative. The isolation of the latter compound, from the *p*-bromotoluene present as an impurity, is evidently due to its readier formation and its greater ability to crystallise.

By the method of Weissberger *et al.* (*loc. cit.*), 58 g. of pure *o*-bromotoluene and 10·6 g. of benzaldehyde yielded 1·3 g. of crystals, which, after recrystallisation from ligroin, gave 0·8 g. (4%) of colourless crystals, m. p. 74—75° (Found : C, 79·7; H, 6·0. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%).

mm'-*Diethoxybenzoin.* This was similarly prepared, 43 g. of *m*-bromophenetole and 9·3 g. of *m*-ethoxybenzaldehyde affording 2·4 g. of uncrystallisable oil; its absorption of oxygen in the autoxidation showed that it contained more than 90% of the acyloin.

Benzoyl-o-chlorophenylcarbinol (o-*Chlorobenzoin*). 60 G. of bromobenzene and 14·5 g. of *o*-chlorobenzaldehyde yielded a product which, after crystallisation from ligroin, was colourless; 12·8 g. (50%), m. p. 82·5—83·5° (Found : C, 68·0; H, 4·6; Cl, 14·7. Calc. for $C_{14}H_{11}O_2Cl$: C, 68·15; H, 4·46; Cl, 14·4%).

We have redetermined the values of the necessary constants at 20° for most of the substances for which data were published before, using freshly prepared material. The new values agree with the earlier ones. The m. p.'s of the following compounds should, however, be corrected : *p*-methylbenzoylphenylcarbinol, 110—111°; benzoyl-*p*-tolylcarbinol, 118—119°; *p*-chlorobenzoylphenylcarbinol, 89·5—90·5°; benzoyl-*p*-chlorophenylcarbinol, 114—115°; benzoyl-*o*-ethoxyphenylcarbinol, 82—83°; oo'-dichlorobenzoin, 63—64°; benzoyl-*o*-tolylcarbinol 68·5—69·5°. Polymorphism seems to be the reason for the (small) deviations from the earlier values. In the case of the *o*-methylbenzoylphenylcarbinol, however, our former values for the autoxidation rate are in error for the reason given above.

52. *Autoxidation Processes. Part IX. The Electrolytic Dissociation of α-Ketols.*

By ARNOLD WEISSBERGER and HERBERT BACH.

THE rates of autoxidation, oxidation with Fehling solution, and racemisation of α-ketols are proportional to the concentrations of alkali in the reacting solutions (Weissberger *et al.*, *Ber.*, 1929, **62**, 1942; 1931, **64**, 1200; *Annalen*, 1930, **478**, 112; **481**, 68; 1933, **502**, 53); this led to the conclusion than an electrolytic dissociation of the ketol is the first step in these processes. Furthermore, a relation has been established (see Part VIII, preceding paper) between the rates of these reactions of the ketols and the dissociation constants of the corresponding carboxylic acids. This seems to indicate that the ability both of the ketol group and of the carboxylic group to undergo electrolytic dissociation is similarly influenced by the radicals attached to them. Exceptions to this relation are found in certain *o*-substituted ketols where steric hindrance comes into play (see Part VIII).

For the further investigation of these phenomena, it seemed desirable to obtain more detailed knowledge about the dissociation of the α-ketols. The method developed for this purpose promises to be useful also for other problems dealing with substances which are insoluble or but sparingly soluble in water.

The small solubility in water of most of the ketols in question prevented measurements in aqueous solution, but ethyl alcohol was a suitable solvent. This excluded potentiometric measurements, as being not sufficiently exact, and also direct determination of the conductivity because this was too small. We therefore measured the decreases in conductivity which a 0·01N-solution of sodium hydroxide in 90% ethyl alcohol undergoes on the addition of the ketols to a concentration of 0·02M.

The significance of these values appears from the following considerations. The conductivity of the aqueous-alcoholic solutions of sodium hydroxide is equal to the sum of the products of the concentration and migration velocity of the ions Na·, HO′, and $C_2H_5O′$. For our solutions, we may further assume that the dissociation of the hydroxide, of the ethoxide in equilibrium with it, and of the sodium salts of the α-ketols is practically complete. Therefore, on the addition of the ketol, the concentrations of sodium ions and of the anions will remain constant. A certain amount of the hydroxide and ethoxide ions, however, will be replaced by the anions of the ketol. The migration velocities of these are considerably smaller than those of the hydroxide and ethoxide ions, but for the different ketols under investigation they may be assumed to be practically the same. The decreases in conductivity, therefore, are the consequence of the replacement of the hydroxide and ethoxide ions by the ketol ions, and are proportional to the concentrations of the latter. Since the total concentration of the ketol in our experiments is high (0·02M), and the fraction dissociated very small, the denominator in the law of mass action which defines the dissociation constants can be taken as constant in our solutions, and therefore the measured decrease is proportional to the dissociation constant. The measurements have been extended to some other comparison substances (p. 228), which may be of use for other purposes.

EXPERIMENTAL.

Measurements.—Conductivities were determined by Kohlrausch's method with induction coil and telephone. The resistance of the Wheatstone bridge (1000 mm. long) was 17·62 ohms : it was extended by a resistance of 200 ohms, so its length was equivalent to 12,290 mm. The minima were well defined within 1 mm. It proved best to use a cell of high constant (1·02); this was made of glass, with electrodes consisting of very thin platinised platinum pins, 1·2 mm. thick and 10 mm. long, about 10 mm. apart. The temperature of the thermostat was 20·0° ± 0·02°. The solvent alcohol was purified from aldehyde according to Danner and Hildebrand (*J. Amer. Chem. Soc.*, 1922, **44**, 2824). The alcoholic sodium hydroxide solution was freshly prepared for each measurement by diluting 20 c.c. of carbonate-free 0·1N-sodium hydroxide (Fixanal) with alcohol to 100 c.c. For the measurement, 25 c.c. of this 0·02N-sodium hydroxide solution were mixed with 25 c.c. of either alcohol or a 0·04M-alcoholic solution of the ketol. The solutions had been previously freed from oxygen by a stream of nitrogen, which was purified

by alkaline pyrogallol solution and red-hot copper and saturated with the vapour of the solvent. For this purpose and for the mixing, we used a round-bottomed flask fitted with a dropping funnel and with tubes for the introduction and the escape of the gas and for transferring the liquid into the conductivity cell. One of the solutions was placed in the flask, the other in the funnel, nitrogen passed through for 20 minutes, then the solutions were mixed by opening the tap of the funnel, stirred by the gas stream, and transferred through the communicating tube to the cell, which was filled with nitrogen. All exit tubes for the gas had liquid seals.

Before each measurement, the apparatus was tested by a measurement of a 0·01N-sodium hydroxide solution; the deviations in these measurements, as well as those of the solutions containing the ketols, which were measured several times, never exceeded 1·5 mm. on the bridge. The differences between the conductivities of the pure sodium hydroxide solutions and the solutions containing the ketols were 17—130 mm. The first measurement was carried out 10 minutes after the mixing. A change in the conductivity after 1 hr.'s standing in the cell was observed only with the chlorobenzoins, but even there it did not exceed 2 mm. on the bridge.

The values given in the last cols. of Tables I—III of the preceding paper are the differences between the conductivity of the 0·01N-sodium hydroxide solution (x) and that of the solutions containing 0·01N-sodium hydroxide and 0·02M-α-ketol (x'). Each value of $x - x'$ is the average of more than one independent measurement.

DISCUSSION.

It must first be emphasised that the benzoins with a *different substituent* in each ring isomerise in alkaline solution to an equilibrium. The rate of this isomerisation can be assumed to be identical with the racemisation velocities of the respective optically active benzoins, because it is highly probable that the intermediate product of both processes is identical. In any case, the isomerisation will not be the faster process. Since the racemis-

FIG. 1.

ation velocities in the cases hitherto investigated (Weissberger *et al., loc. cit.*) are identical with those of the autoxidation, the latter provide the data for the calculation of the amounts to which the benzoins in question will have isomerised before the actual measurements. An uncertainty is introduced into these calculations, however, by the possible influence of the solvent. The autoxidation rates are determined in 79% ethyl alcohol, and the conductivities in 90% alcohol; now the velocity of autoxidation is approximately doubled by a change of solvent from 45% to 79% alcohol (*loc. cit.*), but measurements with benzoin showed that the further increase caused by changing to 90% alcohol is only about 20%. Therefore, the extent of isomerisation before the measurement takes place is less than 5% with the *p*-methyl- and the *o*-ethoxy-benzoins, and less than 20% with the other unsymmetrical benzoins. The smallness of the differences between the values of $x - x'$ for the isomeric benzoins in question, therefore, is genuine and not due to previous isomerisation. This is in agreement with the differences in the autoxidation rates of the " unsymmetrical " benzoins : since the intermediate for the isomerisation reacts completely with the oxygen if the latter is abundant (*Ber.*, 1931, **64**, 1200), no isomerisation can interfere with the autoxidation measurements.

To illustrate the relation between the electrolytic dissociation of the ketols and of the corresponding carboxylic acids, the values of $x - x'$ are plotted against the products of the dissociation constants of the latter in Fig. 1. The points for the *p*-substituted com-

pounds are situated *on one curve*: a variation which alters the dissociation constants of the acids gives rise to a corresponding change in the dissociation of the ketols. The similarity of the groups –CO·OH and –CO·Ç·OH is close enough to provide for this kinship, even though the absolute values of the dissociation constants of the carboxylic acids are about six orders of magnitude higher than those of the ketols.
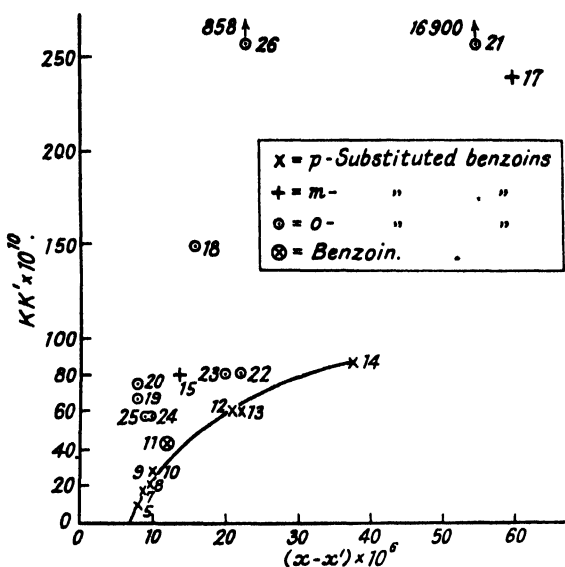
The estimation of the absolute values of the dissociation constants of the ketols is possible from the $x - x'$ values of the substances given below, the electrolytic dissociation constants of which are recorded in the literature. The value of benzophenone-oxime, the molecular size of which is similar to that of the benzoins, shows that when $10^6(x - x') = 50$, the dissociation constant is of the order of 10^{-12}. As to the other two substances, one must bear in mind that their smaller molecular sizes — higher migration velocities—diminish the effect in $x - x'$.

FIG. 2.
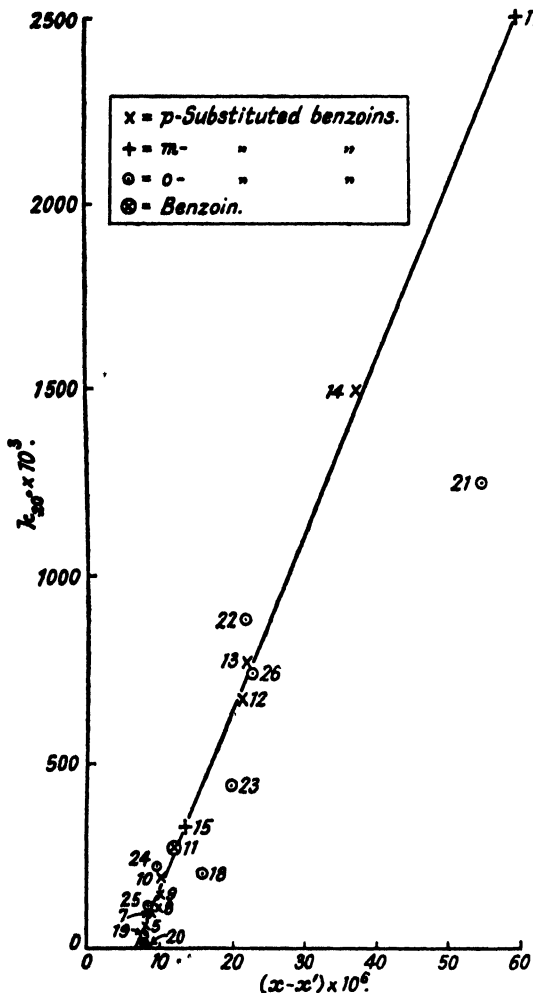
	$(x - x') 10^6$.	K.
Glycol	2·3	6×10^{-15}
Acetoneoxime	20·4	6×10^{-13}
Benzophenoneoxime	55·1	5×10^{-12}

Of the *m*-derivatives, only two have been measured, but a similar curve plotted through them would lie above that for the *p*-substituted substances : introduction of substituents into the *m*-position seems to raise the dissociation of the acids more than that of the ketols. The value for benzoin itself falls between the two curves.

These results are in full agreement with the observation that the ratio of k to K (see p. 224) is smaller with *m*- than with *p*-substituted compounds.

The *o*-substituted compounds give widely scattered points, and the displacement from the curve for the *p*-derivatives is the greater the smaller the ratios in col. 5 (Table III, p. 224), *i.e.*, the greater the effect there characterised as steric hindrance. If, however, we plot $x - x'$ against the *autoxidation rates* (Fig. 2) * a close proportionality is seen to hold between the two properties for all the compounds, including the *o*-deriv-atives : the small deviations with *oo'*-diethoxy- and *oo'*-dimethoxy-benzoin are within the limits of experimental error. It should be remembered that for *oo'*-diethoxybenzoin the close coincidence of autoxidation rate and racemisation velocity (*loc. cit.*) showed that the steric hindrance cannot be attributed to any phase in the autoxidation process which is subsequent to that in which the racemisation occurs. Those deviations, therefore, are without significance for the essential steric hindrance. Even with *oo'*-dimethyl- and *oo'*-dichloro-benzoin, however, the deviations are small in comparison with the amounts under discussion.

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* The rate of autoxidation of *mm'*-dichlorobenzene was too high for direct measurement at 20°, and was calculated from that at 10° with the average temperature coefficient.

It follows that the steric hindrance in autoxidation, oxidation with Fehling solution, and racemisation of the α-ketols takes place in their *electrolytic dissociation*. This may be considered as evidence for the theory of dissociation of acids according to which the process involves the *approach of a molecule or ion*, e.g., AcOH + H$_2$O ⇌ (AcOH$_2$O) ⇌ AcO' + H$_3$O'. It should be pointed out that, as has been shown in Part VIII, not only the size but also the charge of the o-substituents is of importance in steric hindrance : chlorine with its negative field has an exceptionally strong effect. This suggests that the dissociation at least of very *weak acids*, like that of the ketols, involves the approach of a *negative* particle which may be hindered, not only by the volume of a substituent, but also by the electrostatic repulsion of a negative substituent according to the mechanism AcOH + HO' ⇌ AcO' + H$_2$O.

The observation that o-substitution in the ring adjacent to the hydroxyl group is more effective in its hindrance than the same substitution in the other ring, obviously agrees with the interpretation given above.

In subsequent papers there will be discussed the mechanism of the autoxidation and the related processes, and the reason for the failure of the curve in Fig. 2 to pass through the origin.

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53. *Studies in Solvent Action. Part IX. Rotatory Powers of the* l-*Menthyl Esters of* m-*Nitro- and* 3 : 5-*Dinitro-benzoic Acids in Relation to the Solvent, Concentration, Temperature, and Wave-length of Light.*

By ANDREW MCLEAN.

THE molecular rotation of menthyl benzoate is less than that of the three mononitro-benzoates irrespective of the solvent employed (Cohen and Armes, J., 1905, **87**, 1190; Kenyon and Pickard, J., 1915, **107**, 35). In benzene solution, however, although the 2 : 6-dinitro-compound shows a further increase in rotation over that of the o-nitro-compound, yet the rotations of the 2 : 4- and the 3 : 5-dinitro-ester are less than those of the o- and the m-nitro-ester respectively (J., 1906, **89**, 1479). In Part VIII (J., 1934, 351), this somewhat unexpected result was pointed out in connexion with the 2 : 4-dinitro-benzoate, and it was suggested that it might be due to a type of solvent–solute combination. The present paper deals with polarimetric and other investigations on the menthyl esters of m-nitro- and 3 : 5-dinitro-benzoic acids, gives further evidence of the validity of the suggestion previously advanced, and attempts to correlate the data with current theories concerning the effect of solvents on optical activity.

The esters were prepared by heating the acid chlorides with 2 mols. of l-menthol, steam-distilling the excess of menthol, extracting the ester with ether, and working up the extract in the usual way. The m-nitrobenzoate was obtained as a pale yellow, viscous oil of rotation slightly higher than that recorded by Cohen. The 3 : 5-dinitro-ester crystallised from alcohol in long colourless needles, which were rather less soluble in most solvents than the nitrobenzoic esters hitherto employed.

Solvent Effects.—The effect of solvents on the rotatory powers of the two esters is very similar, so they may be considered together (see Table I). The most striking feature revealed by these results is that, with increasing polarity of solvent, the molecular rotation of the solution increases, *i.e.*, the solvent effect usually observed with this type of compound is reversed. A second point is that, although the rotations of the m-nitrobenzoate in benzene and toluene are greater than those of the 3 : 5-dinitrobenzoate, the range of variation of [M]$_\lambda$ is wider in the case of the latter compound, with the result that in solvents of medium and high polarity the dinitro-ester has the higher rotations.

In the course of the previous work (Part VIII) with mono- and di-nitrated menthyl benzoates in solution, evidence was obtained from molecular-weight measurements at

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TABLE I.

Solvent.	Limiting values. α_{6780}	α_{4358}	$[M]_{6708}$	$[M]_{5469}$	$[M]_{5893}$	$[M]_{5469}$	$[M]_{4861}$	$[M]_{4358}$	$\mu \times 10^{18}$ (solvent).
			l-Menthyl *m*-nitrobenzoate ($t = 20°$, $c = 4$ approx., $l = 1$).						
C_6H_6	$-2\cdot70°$	$-7\cdot18°$	$-208\cdot0°$	$-217\cdot2°$	$-268\cdot0°$	$-317\cdot3°$	$-418\cdot2°$	$-553\cdot0°$	0
$C_6H_5\cdot CH_3$	2·79	7·19	210·1	217·6	268·0	317·7	416·5	541·4	0·5
$C_6H_5\cdot O\cdot CH_3$	2·85	7·22	213·3	222·3	280·0	322·7	420·8	540·5	1·25
C_6H_5Br	3·02	8·09	221·5	231·8	286·8	340·4	449·8	593·4	1·50
C_6H_5CHO	3·19	8·62	221·8	232·2	286·4	341·4	451·2	599·4	2·74
$C_6H_5\cdot NO_2$	3·16	*6·57	216·8	227·8	284·1	339·7	450·9	—	3·90
$C_6H_5\cdot CN$	3·12	8·47	231·5	240·3	295·3	353·1	465·9	628·3	3·85
†C_6H_{12}	2·47	6·84	188·6	196·2	242·8	289·4	384·2	522·4	0
			l-Menthyl 3 : 5-dinitrobenzoate ($t = 20°$, $c = 4$ approx., $l = 1$).						
C_6H_6	$-2\cdot21°$	$-5\cdot60°$	$-191\cdot5°$	$-200\cdot2°$	$-247\cdot1°$	$-293\cdot5°$	$-382\cdot2°$	$-486\cdot4°$	0
$C_6H_5\cdot CH_3$	2·35	5·71	204·9	213·6	264·1	309·4	399·2	496·6	0·5
$C_6H_5\cdot O\cdot CH_3$	2·52	6·20	217·6	226·3	279·0	329·1	424·1	535·5	1·25
C_6H_5Br	2·61	7·03	227·9	235·7	295·1	351·0	463·6	613·8	1·50
C_6H_5CHO	2·65	7·45	232·0	244·3	304·8	365·2	487·9	652·6	2·74
$C_6H_5\cdot NO_2$	2·78	*5·94	242·7	255·8	321·2	386·7	518·6	—	3·90
$C_6H_5\cdot CN$	2·90	8·24	250·4	261·6	327·2	391·1	528·5	711·3	3·85
†C_6H_{12}			Ester practically insoluble.						

* α_{4861}.   † C_6H_{12} = *cyclo*Hexane.

increasing concentrations which pointed to the abnormal molecular state of the 2 : 4-dinitrobenzoate dissolved in benzene. This difference, which showed itself, when molecular weight was plotted against concentration, as a maximum followed by a minimum in a region which included the concentration of the polarimetric solutions, was interpreted (cf. Turner, " Molecular Association," pp. 33, 37) as indicating combination between solvent and solute accompanying increasing molecular (dipolar) association of the solute. Accordingly, the molecular weights of the two esters now under discussion were determined ebullioscopically in non-polar solvents of benzenoid and of non-benzenoid character, *viz.*, benzene and *cyclo*hexane respectively; the method employed was that of Menzies and Wright (*J. Amer. Chem. Soc.*, 1921, **43**, 2314). The results are detailed in Table II ·and plotted in Fig. 1.

TABLE II.

m-Nitrobenzoate.   *M*, calc., 305.   3 : 5-Dinitrobenzoate.   *M*, calc., 350.

Solvent, *cyclo*hexane; ebullioscopic weight constant (k) = 28·6.

$W = 20\cdot19$; b.p. = 81·0°. $W = 18\cdot75$; b.p. = 81·2°.

w.	*e.*	*M.*	*w.*	*e.*	*M.*	*w.*	*e.*	*M.*	*w.*	*e.*	*M.*
0·1940	0·090°	306	0·6021	0·269°	317	0·1315	0·057°	352	0·5360	0·207°	395
0·3980	0·180	313	0·7766	0·336	328	0·2462	0·102	368	0·6469	0·249	396
						0·3860	0·155	380			

Solvent, benzene; ebullioscopic weight constant (k) = 26·1.

$W = 22\cdot82$; b. p. = 80·0°. $W = 22\cdot65$; b. p. = 80·2°.

0·1966	0·068	331	0·7298	0·217	385	0·2117	0·065	375	0·8291	0·262	365
0·3483	0·111	359	0·9286	0·287	370	0·4046	0·108	432	1·0427	0·342	351
0·5202	0·161	369				0·6068	0·183	382			

Within the. limits of concentration of the determinations (which cover that of the polarimetric solutions) the solutions fall into two classes : (*a*) those in *cyclo*hexane, in which the shape of the curve is normal for increasing molecular association of solute with increase of concentration, and (*b*) those in benzene, the curves of which may be interpreted, in the same way as before, as showing both molecular association of solute and solvent-solute combination. It is also to be observed that for each ester the curve for *cyclo*hexane lies below the corresponding one for benzene, in one case over the whole range of concentrations and in the other over about half the range. Observation (*b*) suggests that solvent-solute combination tends to show itself as an increase in the measured molecular weight. In his experiments on the molecular weights of metals in mercury, Ramsay (J., 1889, **55**, 521) took this view, arguing that the total effect was the measurement of the molecular weight of the addition compound. Turner (*op. cit.*, p. 37), on the other hand, points out that the action of combination is to be regarded as merely reducing the amount of free

solvent, thereby virtually concentrating the solution and leading to a lower calculated molecular weight since the elevation of the b. p. and depression of the f. p. will be increased. Whilst Turner's objection is probably valid with respect to Ramsay's solutions, in which the proportions of the components were one atom of solute to 25—100 atoms of solvent, it is hardly likely to hold in the present cases, where the ratio is 1 mol. of solute to 2000—4000 mols. of solvent.

The simple theory of dipolar association, solvent–solute combination being ignored, indicates that association of the ester should be greater in *cyclo*hexane than in benzene under the same conditions, for the latter has the higher dielectric constant. It is therefore to be expected that, in cases where dipolar association is the predominant factor over the whole range of concentrations, the curve for *cyclo*hexane solutions will lie above that for benzene solutions. The polarimetric data for the esters already examined (J., 1934, 351) were in agreement with the predictions of the dipolar association hypothesis, so presumably this was the predominant influence; the molecular-weight data accordingly agreed with the above conclusions. However, the two esters now under discussion seem to show no agreement with the predictions of the simple theory of dipolar association in respect to their polarimetric behaviour. It is therefore not surprising that the diagrams for molecular weight against concentration are

FIG. 1.

also displaced in comparison with those already obtained. It seems reasonable to assume that molecular combination between solvent and solute is the predominant factor in the present binary systems.

Hitherto, in discussing the effect of solvents on optically active molecules, orientation of the permanent dipoles as depicted in the inset has been sufficient to explain the majority of the effects observed. However, it was at no time assumed that this mechanism represented completely the influence of solvents, and evidence of other operative factors was sought. Now that the formation of addition compounds in optically active solutions, which exhibit rotations different from those expected on the above mechanism, has been established with some degree of certainty, an indication is forthcoming of the direction in which further influences may be found.

The following structural formulæ emphasise the polar nature of the substances which have been found to form addition compounds with benzene and at similar concentrations show abnormal rotatory powers in benzenoid solvents :
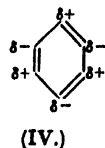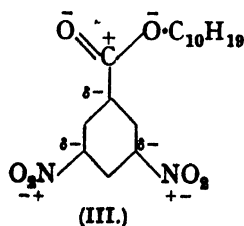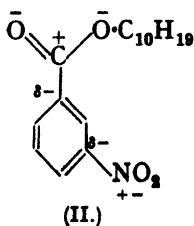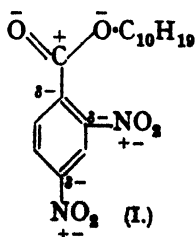
(I.)   (II.)   (III.)   (IV.)
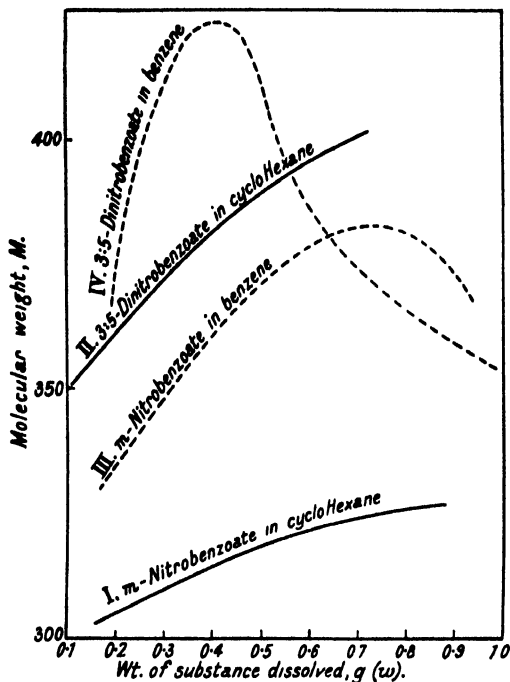
The benzene nucleus in (III) is nearly electrically symmetrical; in (II), the two polar groups both tend to induce a negative charge on the carbon atom in position 5, so that the aromatic ring is again approaching electrical symmetry; in (I), the total effect of the substituent groups is to induce a negative charge on the carbon atom in position 6, but the electrical symmetry of the benzene ring in this molecule probably will be much less than that of (II) or (III). Taken in conjunction with the fact that the curves for the molecular weight plotted against concentration demonstrate that the formation of addition compounds is less with (I) than with (II) and (III), this reasoning leads to the conclusion that electrical symmetry of the optically active molecule is a significant factor in addition-compound formation.

How, then, may this formation take place between benzene and molecules of the types (I), (II), and (III) in order to affect the rotation of the latter? The benzene molecule is non-polar, and so could not take part in an association involving permanent dipoles, but consisting, as it does, of a symmetrical ring of conjugated double bonds, it is easy to imagine such a system becoming polarised by induction as in (IV) on the approach of molecules of the electrical types (I), (II), or (III). The formation of molecular compounds between the two components could then take place by hexapolar association, which would not differ in essence from dipolar association, but would involve a greater degree of orientation of the component molecules with respect to each other. The strength of such a union would probably depend on the symmetry of the electrical field of the aromatic nucleus in the ester molecule and, therefore, the order of stability of the addition compounds, $(III),C_6H_6>(II),C_6H_6>(I),C_6H_6$, is to be expected. The decrease in rotatory power of the ester molecules due to hexapolar association will, accordingly, be in the order $(III)>(II)>(I)$.*

With the introduction of a substituent into the benzene ring, the whole structure of the solvent molecule becomes electrically unsymmetrical owing to repulsion or attraction of electrons, *i.e.*, the substituent exerts a controlling influence on the electrons in other parts of the ring. This controlling influence will be proportional to the polarity of the entering group. As a result, the polarisation of the electrons by a system of charges outside the molecule will be less facile than in the unsubstituted benzene molecule. By application of this reasoning to binary liquid systems such as solutions of molecules (I), (II), or (III) in pure monosubstituted benzenes containing substituents of increasing polarity, it follows that the induced polarisation of the solvent ring by the solute molecule will decrease as the polarity of the substituent in the solvent molecule increases; consequently, compound formation of the above type between solute and solvent will decrease in the same manner. Thus the lowering of the rotations of molecules (I), (II), and (III) due to compound formation would be greatest in benzene solution, less in solvents of intermediate polarity, and least in strongly polar solvents such as nitrobenzene and benzonitrile.

The conclusion may therefore be drawn, that, with the optically active esters now being discussed, hexapolar association alone would lead to the highest rotations being observed in strongly polar solvents, and the lowest in non-polar solvents. However, association of the permanent dipoles has also to be taken into consideration, and the evidence already recorded in this series of papers makes it practically certain that the effect of this factor with this type of solute will be exactly the reverse of that of hexapolar association. In the absence of other dominant influences, the relative strengths of these two factors will determine the order of the rotations in a series of similar solvents derived from the same hydrocarbon. It would seem that solutions of the *m*-nitro- and 3 : 5-dinitro-benzoates present particularly good examples of systems where hexapolar association is predominant; the increasing influence of dipolar association with increase in strength of the solvent dipole is seen, however, in both cases with nitrobenzene solutions, the rotations of which tend to fall amongst the values for solutions in solvents of inter-

* It is of interest that Briegleb (*Z. physikal. Chem.*, 1934, *B*, **26**, 63), as a result of his work on the molecular complexes formed between nitro-compounds and hydrocarbons, has deduced a mechanism which is essentially the same as that outlined above.

mediate polarity. Dipolar association, on the other hand, is apparently the predominant influence in solutions of the 2 : 4-dinitrobenzoate; this is not unexpected, for the 2-nitro-group has the largest effect on the rotatory power, and the data for the *o*-nitrobenzoate show that this group is very sensitive to changes of polarity in the solvent. However, hexapolar association would seem to be fairly strong at the non-polar end of the solvent series, with the result that solutions in such solvents have lower rotations than solutions of the *o*-nitrobenzoate in the same solvents.

The 3 : 5-dinitrobenzoate is much less soluble in benzenoid solvents than the other mono- and di-nitrated menthyl benzoates previously investigated, and for this reason the argument might be advanced that it does not form molecular compounds with these solvents. On the other hand, its solubility in benzenoid solvents is very much greater than in solvents of other types, *e.g.*, alcohol, *cyclo*hexane, and decalin. Furthermore, the 3 : 5-dinitrobenzoate differs strikingly in crystalline form from the other esters, and its m. p. is 80—90° higher than those of the latter, both of which facts suggest that its comparatively low solubility is due to greater strength of intracrystalline forces rather than to small affinity for benzenoid molecules. Finally, the *m*-nitrobenzoate, which is analogous to the 3 : 5-dinitrobenzoate in rotatory power and molecular-weight peculiarities, is a liquid and is very soluble in all benzenoid solvents.

The application of these ideas to the results obtained with other optically active substances in solution is obvious, for, if the effects of dipolar association and combination with the solvent happened to be nearly equal and opposite, then a solvent series showing little or no regular variation of rotation with polarity of solvent is to be expected. On the other hand, the converse of this statement is not necessarily true, for other factors may be active in masking regularities (*e.g.*, formation of co-ordinate linkages; Rule, Smith, and Harrower, J., 1933, 376). Further, it is not to be expected that dipolar association and combination with the solvent will always have opposing effects on the rotation of an optically active solute. This has been shown to be probable when the optically active molecule contains a substituent which increases the rotation of the un-substituted compound but, if the substituent causes the rotation to be lower than that of the latter, the above effects may be expected to aid one another. It is difficult to obtain a substituent which lowers the rotation of the unsubstituted compound and has a polarity comparable with that of the nitro-group whilst remaining chemically inert towards the solvent, but it is proposed to carry out investigations with the menthyl dimethylamino-benzoates in an attempt to elucidate further the points raised.

TABLE III.

Effect of concentration.

Solvent	c.	Limiting values.		$[M]_{6708}$	$[M]_{5893}$	$[M]_{5893}$	$[M]_{5463}$	$[M]_{4861}$	$[M]_{4358}$
		a_{6708}	a_{4358}						
l-Menthyl *m*-nitrobenzoate ($t = 20°$, $l = 1$).									
C_6H_6	3·960	−2·70°	−7·18°	−208·0°	−217·2°	−268·0°	−317·3°	−418·2°	−553·0°
„	8·146	5·61	14·90	210·1	218·6	270·3	321·3	423·2	558·0
„	16·504	11·27	30·12	208·2	217·2	269·5	320·1	420·9	556·8
„	31·866	21·63	57·53	207·0	215·6	267·5	317·6	417·6	550·5
„	63·748	43·51	*66·06	206·5	214·4	266·0	316·1	—	—
$C_6H_5·NO_2$	4·444	3·16	§6·57	216·8	227·8	284·1	339·7	450·9	—
„	7·956	5·63	§11·69	215·8	225·0	281·4	337·0	448·2	—
„	17·896	12·46	§25·76	212·3	221·6	276·8	330·7	438·8	—
„	32·722	22·12	§46·00	206·2	216·4	270·3	322·5	428·9	—
l-Menthyl 3 : 5-dinitrobenzoate ($t = 20°$, $l = 1$).									
C_6H_6	4·030	2·21	5·60	191·5	200·2	247·1	293·5	382·2	486·4
„	8·056	4·49	11·37	195·1	202·5	249·8	295·5	384·9	494·0
„	9·840	5·50	14·03	195·7	203·5	251·4	297·3	388·1	499·0
$C_6H_5·NO_2$	4·009	2·78	§ 5·94	242·7	255·8	321·2	386·7	518·6	—
„	8·042	5·53	§11·74	240·7	252·0	316·3	379·8	511·0	—

* a_{5463}.   § a_{4861}.

TABLE IV.

Effect of temperature.

Limiting values.

Solvent.	$d_r^{4°}$.	Temp.	a_{6708}.	a_{4358}.	$[M]_{6708}$.	$[M]_{4358}$.	$[M]_{5893}$.	$[M]_{5463}$.	$[M]_{4861}$.	$[M]_{4358}$.
l-Menthyl *m*-nitrobenzoate ($l = 1$; $p = 3\cdot487$ in decalin, $= 4\cdot444$ in $C_6H_5\cdot NO_2$).										
Decalin	0·8890	20·0°	−2·16°	−5·39°	−212·5°	−222·3°	−274·4°	−323·7°	−414·2°	530·2°
,,	0·8733	40·8	2·12	5·32	212·3	222·3	275·4	324·5	416·7	532·9
,,	0·8604	58·3	2·08	5·22	211·4	221·6	275·5	324·3	417·8	530·6
,,	0·8453	78·6	2·02	5·12	209·0	218·2	272·0	320·7	414·8	529·6
,,	0·8317	97·0	2·00	5·07	210·3	220·8	273·4	324·9	419·6	533·1
$C_6H_5\cdot NO_2$	1·1795	39·5	2·99	§6·17	208·5	217·7	272·7	325·7	430·3	—
,,	1·1614	58·5	2·85	§5·90	201·9	210·4	264·2	315·3	418·0	—
,,	1·1241	78·0	2·71	§5·66	195·2	203·8	257·1	307·5	407·6	—
l-Menthyl 3 : 5-dinitrobenzoate ($l = 1$; $p = 3\cdot334$).										
$C_6H_5\cdot NO_2$	1·2027	20·5	2·78	§5·94	242·7	255·8	321·2	386·7	518·6	—
,,	1·1842	39·5	2·66	§5·59	235·8	247·4	309·4	370·7	495·7	—
,,	1·1659	58·2	2·52	§5·28	226·9	238·5	297·1	355·6	475·3	—
,,	1·1452	79·5	2·40	§4·99	220·1	229·2	288·8	347·5	457·6	—
,,	1·1253	99·8	2·26	§4·78	211·0	220·3	277·3	336·1	446·2	—

§ a_{4861}.

Concentration and Temperature Effects.—As far as possible, the procedure formerly adopted was adhered to, the effects of concentration and of temperature being measured in a non-polar and in a polar solvent in each case. The results are set forth in Tables III and IV. (Owing to the extremely slight solubility of the 3 : 5-dinitrobenzoate in decalin, the temperature effect could not be determined.)

FIG. 2.
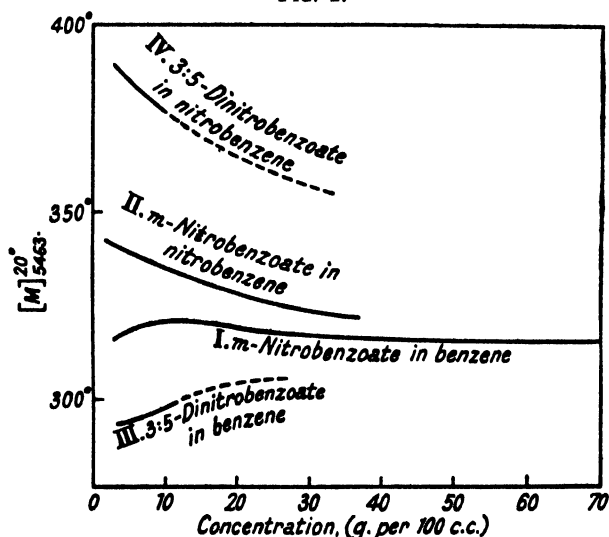
In Fig. 2 the values of $[M]_{5463}$ from Table III are plotted against the corresponding concentrations; the resulting curves are shown in full lines. The shapes of the curves are very much those which might be expected if the assumptions already made are valid. The right-hand half of Curve III, Fig. 1, corresponds to 2—4% solutions of the *m*-nitrobenzoate in benzene, and at this concentration combination between solvent and solute is extensive; Curve I, Fig. 2, shows that the rotation of this ester in benzene reaches a low value in this same region. Unfortunately, the ebullioscopic molecular-weight apparatus did not allow the use of greater concentrations of *m*-nitrobenzoate, but from the shape of the corresponding curve for the 2 : 4-dinitrobenzoate (J., 1934, 357), it may be inferred that Curve III, Fig. 1, will, at greater concentrations, reach a minimum and again rise

normally, indicating that combination with the solvent becomes relatively less extensive. Correspondingly, Curve I, Fig. 2, rises to a maximum and then falls with increasing concentration towards the value for the homogeneous ester ($[M]_{5461}^{20^\circ} = -300^\circ$). Curve II, for the *m*-nitrobenzoate in nitrobenzene, exhibits a normal trend over the concentration region investigated, *viz.*, an approach towards the rotation value of the homogeneous ester as the concentration increases; no maximum is apparent, indicating that compound formation between the ester and nitrobenzene is inappreciable. The 3 : 5-dinitrobenzoate is a much more difficult compound with which to obtain sufficient data, owing to its slight solubility and to its high m. p., which prevents the determination of its rotation in the homogeneous state. So far as such investigations were possible, however, they indicate that its behaviour is similar to that of the *m*-nitrobenzoate, and the dotted extrapolations of the curves are probably justified.

In a discussion of the changes in optical rotation predictable by the dipole-association hypothesis, Rule, Barnett, and Cunningham (J., 1933, 1217) concluded that " the temperature–rotation curve for a strongly polar solvent should converge towards that of a non-polar medium as the temperature rises," and also that " in position and direction, the temperature–rotation curve for the homogeneous compound will lie between those observed for solvents of the extreme types." Patterson and co-workers (J., 1908, **93**, 1836, and later) regard the problem of variation of rotation with temperature from a different angle, and conclude that experimentally determined temperature–rotation curves are merely parts of a general temperature–rotation curve the whole of which should theoretically be able to be reproduced by suitable changes of solvent, wavelength, temperature, and substituent in the optically active molecule. From this generalisation, it is deduced that, according as the rotation in a given solvent is much below or above that of the homogeneous optically active compound, rise in temperature will respectively raise or diminish the rotation (or cause it to increase very slowly in the latter case). In Part VIII (*loc. cit.*),

FIG. 3.

I.   *m-Nitrobenzoate (homogeneous)*.
II.   ,,   *in nitrobenzene*.
III   ,,   *in decalin*.
IV. 3 : 5-*Dinitrobenzoate in nitrobenzene*.

it was shown that solutions in which dipole association was predominant, *viz.*, solutions of menthyl *o*-nitro- and 2 : 4-dinitro-benzoates, conformed to the conclusions of Rule, Barnett, and Cunningham, whereas solutions showing no regular variation of rotation with the dipole moment of the solvent obeyed Patterson's rule.

The results of the present investigation for one of the wave-lengths employed are set forth graphically in Fig. 3; the values for the homogeneous *m*-nitrobenzoate for λ = 5461 are due to Kenyon and Pickard (J., 1915, **107**, 35). Considering Curves I, II, and III together, one sees that Patterson's deduction is substantiated; the rotations of both decalin and nitrobenzene solutions are above the homogeneous value, and with rise in temperature the decalin value remains practically constant whilst the nitrobenzene value approaches that of the homogeneous ester. The convergence of Curves I and II agrees with Rule's conclusions, but the relative positions of the three curves are not in accord with those conclusions. Curve IV, by itself, adds little to our knowledge of the problem of the effect of concentration, but, in so far as it runs practically parallel to Curve II, it emphasises the general resemblance between the *m*-nitro- and 3 : 5-dinitro-benzoates.

From the data for the five menthyl esters of nitro- and dinitro-benzoic acids detailed in the present and the preceding papers of this series, the following conclusions with respect to the effect of temperature may be drawn. (1) When dipolar association is the predominant factor influencing rotatory power, the generalisations of Rule, Barnett, and Cunningham offer the best indications of the trends of the temperature–rotation curves. (2) When other factors exert forces of the same order as the dipolar association—
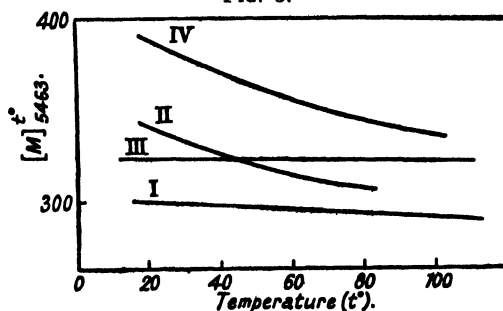
probably an irregular solvent series will be obtained—Patterson's deduction allows of a surer prediction of the relative directions of the temperature–rotation curves.

Optical Rotatory Dispersion.—On plotting $1/\alpha$ against λ^2, a smooth curve showing a regular deviation from linearity is obtained in each case. These curves are of the form usually associated with a dispersion equation such as $\alpha = k_1/(\lambda^2 - \lambda^2) \pm k_2/\lambda^2$, but the constants in this equation could not be calculated from the data available. It would seem that the complexity of the dispersion of the esters now being discussed is greater than that of the isomeric esters previously examined; this is not surprising in view of the other evidence of molecular complexity set forth above. Facilities for a more extensive examination over a wider range of wave-lengths were not available, so the possibility of anomalous dispersion and conformity to a four-constant dispersion equation could not be investigated.

SUMMARY.

(1) Solutions of the menthyl esters of *m*-nitro- and 3 : 5-dinitro-benzoic acids in benzenoid solvents show rotatory powers which vary in a similar manner to the dipole moment of the solvent.

(2) An attempt is made to connect these results with the hypothesis of solvent effect advanced in this series of papers.

(3) The effects of concentration and temperature are discussed in the light of current theories.

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54. *Mechanism of Substitution at a Saturated Carbon Atom. Part III. Kinetics of the Degradations of Sulphonium Compounds.*

By JOHN L. GLEAVE, EDWARD D. HUGHES, and CHRISTOPHER K. INGOLD.

RECENTLY, Hughes, Ingold, and Patel (J., 1933, 526)* considered the mechanism of substitutions of the form

$$Y + Alk\vdots—X \longrightarrow Alk—Y + X \quad . \quad . \quad . \quad . \quad . \quad (S_N)$$

These substitutions are characterised, as the position of the dotted line in the equation indicates, by electron transfers from Y to Alk and from Alk to X; but, subject to this, no restriction is necessary concerning the states of electrification of the species involved. Thus, the reagent Y may be either negatively charged or neutral, and the group X either positively charged or neutral. Whatever the electrical distribution may be, the form of the change is the same, as may be seen by a comparison of such examples as the following :

$$(a) \quad \overset{-}{O}H + Alk·Br \longrightarrow Alk·OH + \overset{-}{Br}$$

$$(b) \quad NMe_3 + Alk·Cl \longrightarrow Alk·\overset{+}{N}Me_3 + \overset{-}{Cl}$$

$$(c) \quad \overset{-}{O}H + Alk·\overset{+}{S}Me_2 \longrightarrow Alk·OH + SMe_2$$

Evidently such differences in electrical distribution are trivial in relation to the fundamental analogy of the examples; consequently the essentials of any general theory of mechanism must apply to *all* substitutions covered by equation (S_N), independently of the electrical distribution. There is reason to believe that the general applicability of the considerations

* This paper will be referred to as Part I of the present series, and the subsequent paper by Hughes and Ingold (J., 1933, 1571) as Part II.

advanced by Hughes, Ingold, and Patel may have been obscured by the circumstance that all their illustrations related to substitutions having the distribution of charges shown in example (*c*). Therefore, we mention the matter at the outset, as the illustrations now to be considered continue to be drawn from the same field.
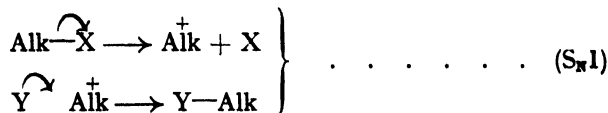
The essential characteristic of equation (S_N) is that the substituting agent is nucleophilic. The reactions collectively represented by this equation may conveniently be called " nucleophilic substitutions."

Concerning these substitutions, Hughes, Ingold, and Patel's main conclusions were (1) that two types of mechanism may operate, (2) that these may be distinguished kinetically, and (3) that it is possible to tell theoretically how the control of a particular substitution by one mechanism or the other should be affected by the chemical constitutions of the interacting species.

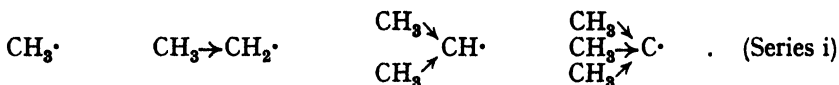The first of the two mechanisms operates in a single stage, which may be formulated thus :

$$Y \quad Alk—X \longrightarrow Y—Alk + X \qquad . \quad . \quad . \quad . \quad (S_N2)$$
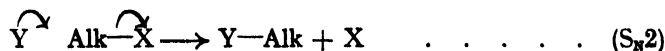
This is a bimolecular reaction. In the second mechanism the process becomes split up into two stages, thus :

$$\left.\begin{array}{l} Alk—X \longrightarrow \overset{+}{Alk} + X \\[2mm] Y \quad \overset{+}{Alk} \longrightarrow Y—Alk \end{array}\right\} \qquad . \quad . \quad . \quad . \quad . \quad (S_N1)$$

It is usually true that the second stage can be treated as instantaneous in comparison with the first, the whole reaction being of the first order. The two mechanisms were regarded as the extremes of a graded range.

In Part I a number of predictions were made concerning the effect of constitutional changes on the mechanism and kinetics of nucleophilic substitutions. Illustrating in the series in which the group X is $\overset{+}{N}Me_3$, the effects were considered which are to be expected from independent variations of the group Alk and the reagent Y. The significant property of the group Alk was shown to be its electron-releasing power, and the effect of progressively increasing the electron repulsion, *e.g.*, by traversing the following series, was discussed :

$$CH_3 \cdot \qquad CH_3 {\rightarrow} CH_2 \cdot \qquad \begin{array}{c} CH_3 \searrow \\ CH_3 \nearrow \end{array} CH \cdot \qquad \begin{array}{c} CH_3 \searrow \\ CH_3 {\rightarrow} C \cdot \\ CH_3 \nearrow \end{array} \qquad \text{(Series i)}$$

This effect is evidently to impede the access of the reagent necessary for mechanism (S_N2),* and to facilitate the ionisation necessary for mechanism (S_N1). Accordingly, on traversing the series from left to right a change of mechanism in the sense $S_N2 \longrightarrow S_N1$ should be experienced if the range of variation of electron repulsion is sufficient. This change of mechanism should be detectable as a change in the reaction kinetics.

Similarly, the significant property of the reagent Y was shown to be its nucleophilic character, of which basicity may be taken as a sufficient indication. The more pronounced the nucleophilic character of the reagent, the more will mechanism (S_N2) be favoured at the expense of (S_N1). Therefore, if a series of reagents is arranged in order of decreasing basicity, *e.g.*,

$$OH' \qquad OPh' \qquad CO_3'' \qquad OAc' \qquad Cl' \qquad . \quad . \quad . \quad \text{(Series ii)}$$
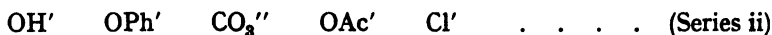
a change of mechanism in the sense $S_N2 \longrightarrow S_N1$ should be experienced on progressing through the series. This change also should be observable by means of the altered reaction kinetics.

It was also foreseen that these changes of mechanism should be associated with certain regular changes of velocity. Considering, first, constitutional variations in the molecule in which the substitution is to occur, the expected relationship is of the following kind. For given physical conditions (see below), the absolute velocity of reaction by mechanism

* It must also impede extension of the vulnerable bond, but this effect is a minor one except for some highly extensible bonds such as are prone to participate in mechanism S_N1.

(S_N2) should continuously decrease, and the velocity of mechanism (S_N1) should continuously increase on traversing series (i) from left to right. If the velocities are plotted as ordinates, the series of groups Alk being set out on the axis of abscissæ, the curves traced should have the general form indicated in Fig. 1. The point of intersection of the curves is the point of change of mechanism. The upper curve on either side of this point is the experimentally realisable curve (see, however, Part IV, p. 249), so that the observed velocity must pass through a minimum. Thus an approach towards the critical point from either side is associated with a continuous decrease of velocity.

The velocity relations determined by constitutional changes in the substituting agent Y are rather different. The form of the velocity diagram of series (ii) is shown in Fig. 2. The curve for mechanism (S_N2) descends with decreasing basicity of the reagent, but in mechanism (S_N1) the reagent is excluded from the slow stage, and the corresponding velocity curve is therefore horizontal. The point of intersection of the curves again marks the change of mechanism. Proceeding towards less basic reagents, the velocity decreases to the critical point, and thereafter remains constant.

It will be evident that in each of these series the precise location of the critical point will depend on the physical conditions; a high concentration must favour mechanism (S_N2). The curves for mechanism (S_N2) can obviously be displaced in a vertical direction by changing the concentration, although the practicable limits within which this is possible
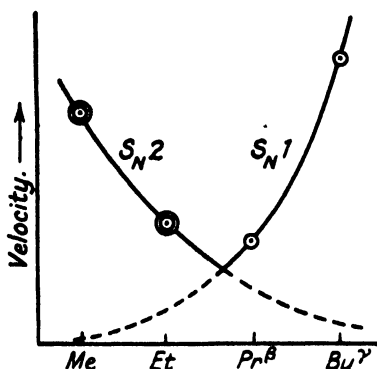
FIG. 1. FIG. 2.
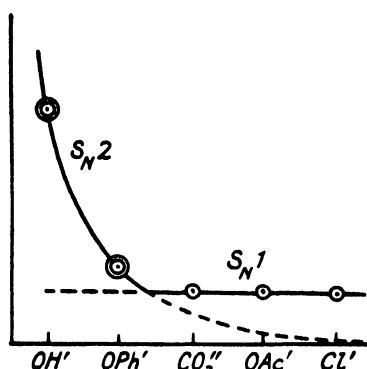
may not suffice to shift the critical point a whole place in the chemical series. Similarly, the solvent must exert a specific effect on each mechanism (see following paper), so the critical point should be capable of displacement by changing the solvent. Finally, it may be recalled that in border-line cases, in which the kinetics are intermediate or definitely dependent on the physical conditions, Hughes, Ingold, and Patel envisaged intermediate mechanisms, rather than a superposition of the extremes : there must be *degrees* of collaboration by the reagent in the process of expelling the substituent that is to be replaced.

At the time of these predictions, no dynamical evidence was available in relation to either of the series illustrated (i and ii). We therefore undertook kinetic studies in each of the three fields of nucleophilic substitutions illustrated by equations (*a*), (*b*),~ and (*c*). As the measurements within field (*c*) have now reached a stage at which it is possible to give a complete confirmation of the predictions of Part I, we report them. The reactions studied are of the form $\overset{-}{X} + Alk \cdot \overset{+}{S}R_2 \longrightarrow X \cdot Alk + SR_2$, and we have not only observed the anticipated change of kinetics in series (i) and series (ii), but have also located the mechanistic critical point in each series, and verified the corresponding velocity relations.

In the series of experiments of which the object was to test the kinetic effect of varying the group Alk as in series (i), the reagent X was always the hydroxide ion : the compounds were trialkylsulphonium hydroxides.

The decomposition of trimethylsulphonium hydroxide is unidirectional, and the products are methyl alcohol and dimethyl sulphide. The kinetics were studied in aqueous solution at 100°. The reaction was shown to be bimolecular with respect to the sulphonium com-

pound. The tests relating to initial velocity and half-life period were satisfied, and the bimolecular equation expressed the course of the change, except that the constant showed a slight upward drift. The magnitude of this is not greater than can be accounted for by the neglect of the activity correction appropriate to an interaction between unlike ions. Experiments carried out in the presence of additional hydroxide ions led to a more detailed specification of kinetics : they showed the reaction to be of the first order with respect to each of the ions of the sulphonium hydroxide. In contrast to an example considered later, the order of the reaction remained the same at the greatest dilutions for which accurate measurement was possible. The replacement of the solvent water by ethyl alcohol in successively increasing proportions led to large progressive increases in the reaction velocity.

It has already been shown (Ingold and Kuriyan, J., 1933, 991) that triethylsulphonium hydroxide in aqueous solution decomposes in two directions, the products being ethyl alcohol and ethylene together with diethyl sulphide. The measurements now reported prove that the total decomposition is bimolecular, and is of the first order with respect to each of the participating ions. We may conclude that this statement applies to the component decompositions separately. The velocity of the total decomposition is increased when the solvent water is replaced by ethyl alcohol.

A comparison of the absolute rates of the decompositions considered in the two preceding paragraphs shows that the reaction leading to the formation of ethyl alcohol proceeds much more slowly than that yielding methyl alcohol.

In dilute aqueous solution methyldi*iso*propylsulphonium hydroxide decomposes substantially in a single direction, the products being *iso*propyl alcohol and the complementary sulphide. Kinetic investigation showed that this reaction is unimolecular. Furthermore, the addition of extraneous hydroxide ions had no effect on the speed ; and even the removal of these ions altogether by replacement with another anion (iodide) was without influence. It follows that the decomposition is of the first order with respect to the sulphonium cation, and that the rate-determining stage proceeds without intervention by the reagent anion. In more concentrated solution, and especially if part of the solvent water is replaced by alcohol, a bimolecular reaction supervenes, but at least a part of this is the elimination process leading to propylene.

The experimental particulars relating to the final member of the alkyl series have already been recorded (Part II, *loc. cit.*). The results show that dimethyl-*tert.*-butyl-sulphonium hydroxide in aqueous solution decomposes mainly in one direction yielding *tert.*-butyl alcohol and dimethyl sulphide, that this reaction is unimolecular even in moderately concentrated solution, and that the speed cannot be altered by the addition of extraneous hydroxide ions or by completely replacing these ions by different anions. This reaction also is accelerated by replacing water by alcohol as solvent.

A comparison of the absolute velocities of the decompositions referred to in the two preceding paragraphs shows that the reaction leading to *tert.*-butyl alcohol takes place very much more rapidly than that yielding *iso*propyl alcohol.

These four sets of experiments show that, for the reaction studied, the point of mechanistic change in series (i) lies between the ethyl and the *iso*propyl group. Moreover, the reaction velocities exhibit the expected relationship (Fig. 1) for a critical point in this position.

In the series of experiments to elucidate the effect of changing the substituting agent as in series (ii), the structure taken for substitution was always the trimethylsulphonium cation, its salts with different anions being investigated.

It has already been noted that the decomposition of trimethylsulphonium hydroxide yields only methyl alcohol and dimethyl sulphide, that the reaction is bimolecular, and that the replacement of solvent water by successively increasing proportions of ethyl alcohol causes a marked increase of speed without any change of kinetic type. For experimental convenience the reaction in alcohol as solvent was taken as the starting point for the present comparisons.

Trimethylsulphonium phenoxide decomposes in a simple manner yielding anisole and dimethyl sulphide. The change was found to be bimolecular in ethyl alcohol, and was shown, by the addition of extraneous phenoxide, to be of the first order with respect to each of the

participating ions. Comparison of the decompositions of trimethylsulphonium hydroxide and phenoxide shows that the latter compound reacts much more slowly than the former.

The decomposition of trimethylsulphonium carbonate in ethyl alcohol was found to be unimolecular, and the speed of reaction was not increased by addition of extraneous carbonate. It follows that the decomposition is of the first order with respect to the sulphonium cation, and that the rate-determining stage does not involve the anion.

The decomposition of trimethylsulphonium chloride was studied in ethyl alcohol and found to be unimolecular also. Von Halban examined the conversion of the bromide into ethyl bromide and diethyl sulphide in a large number of solvents (*e.g.*, alcohol, acetone) and observed unimolecular kinetics in all cases (*Z. physikal. Chem.*, 1909, **67**, 129). This result has been confirmed for a number of further solvents by Essex and Gelormini (*J. Amer. Chem. Soc.*, 1926, **48**, 882) and by Corran (*Trans. Faraday Soc.*, 1927, **23**, 605). Our experiments showed that, for the same temperature and the same solvent, the rates of decomposition of trimethylsulphonium carbonate, bromide, and chloride were identical to within the limits of experimental precision.

It follows from the last five sets of experiments that for the reaction examined the point of mechanistic change in series (ii) lies between the phenoxide and the carbonate ion. Furthermore, the absolute reaction velocities have the relationship expected (Fig. 2) for a critical point in this situation.

A summary of velocity coefficients is appended. The bimolecular coefficients, k_2, are in litres/mol.-hour, and, on account of the appreciable effect of ionic strength on this constant, are quoted for concentrations in the neighbourhood of $0.1M$. The unimolecular coefficients, k_1, are in hours^{-1}.

Summary of Velocity Coefficients (at 100°).

Substitutions.

Cation series. (Solvent : H_2O. Anion : OH′.)				Anion series. (Solvent : EtOH. Cation : $Me_3S^{\cdot}$.)			Solvent effect. ($Me_3S\cdot OH$ in aq. EtOH.)	
Alcohol.	Cation.	k_2.	k_1.	Anion.	k_2.	k_1.	EtOH, % by vol.	k_2.
MeOH	$Me_2S^{\cdot}$	0·133	—	OH′	2670	—	0	0·133
EtOH	$Et_2S^{\cdot}$	0·014	—	OPh′	48	—	60	5·44
$Pr^{\beta}OH$	$MePr^{\beta}_2S^{\cdot}$	—	0·0079	CO_3''	—	0·265	80	64·0
$Bu^{\gamma}OH$	$Me_2Bu^{\gamma}S^{\cdot}$	—	20·5 *	Br′	—	0·279	100	2670
	(* Part II, *loc. cit.*)			Cl′	—	0·263	(Cf. also Part II.)	

For $MePr^{\beta}_2SI$ in water, $k_1 = 0.0071$.

Olefin eliminations.

(Solvent : Aqueous EtOH.)

EtOH, % by vol.

Substance	0	60	80	
$Et_2S\cdot OH$	0·087	7·55	73·8	$\rbrace k_2$
$MePr^{\beta}_2S\cdot OH$	—	6·76	—	

EXPERIMENTAL.

Preparation of Materials.—Dimethyl sulphide, b. p. 37°, prepared by Klason's method (*Ber.*, 1887, **20**, 3412), and methyl iodide were allowed to react in absolute ethyl alcohol; the sulphonium iodide was precipitated with ether and crystallised several times from alcohol, m. p. 215° (decomp.) (Found : I, 62·3. Calc. : I, 62·6%); it was converted into the hydroxide, carbonate, chloride, or bromide by treatment with the corresponding silver salt. An alcoholic solution of the phenoxide was prepared from the chloride with the aid of alcoholic sodium phenoxide, the precipitated sodium chloride being removed.

Diethyl sulphide, b. p. 92°, also prepared by Klason's method, was combined with ethyl iodide in nitromethane solution, and the sulphonium iodide, m. p. 150°, was purified by repeated precipitation first from ethyl alcohol and then from acetonitrile, by addition of ether (Found : I, 51·0. Calc. : I, 51·3%). The picrate had m. p. 149°. The hydroxide was prepared with the aid of silver oxide.

Diisopropyl sulphide, b. p. 118°, was prepared by a method, the details of which were kindly given to us by Dr. F. G. Mann. Its methiodide, prepared in nitromethane solution, and purified by repeated precipitation from acetone by means of ether, had m. p. 161° (Found : I, 47·9.

Calc. : I, 48·8%). The *picrate* had m. p. 161° (Found : C, 43·2; H, 5·3; N, 11·8. $C_{12}H_{18}O_3N_3S$ requires C, 43·2; H, 5·3; N, 11·6%).

Kinetic Measurements.—Methods. Four solvents were employed, *viz.*, water, 60% and 80% (by vol.) aqueous ethyl alcohol, and absolute ethyl alcohol. The alcohol was dried by Lund and Bjerrum's method (*Ber.*, 1931, **64**, 210). The temperature was 100° in all cases.

For each run a number of small, thin-walled, glass tubes, each containing measured portions of the original solution, were heated in a boiling water-bath, and at successive intervals of time a tube was removed, quickly cooled, and cleansed externally by washing with dilute hydrochloric acid (to remove any " hardness " deposited by the water-bath), water, and distilled water. Its contents were estimated volumetrically.

Hydroxides were titrated with phenolphthalein as indicator, phenoxides with lacmoid, and carbonates with Sofnol No. 1, these last estimations being carried out in a stream of air. Chlorides and bromides were titrated by Volhard's method. Iodides were estimated by allowing the alkyl iodide to hydrolyse completely and then titrating the hydriodic acid by means of alkali.

For reactions with half-change periods above 1 hr., the time of commencement of the reaction was taken to be the time at which the tubes were put into the bath; and the initial concentrations were taken to be those of the original solution. For reactions with half-change periods between 1 hr. and 4 mins., a time 1 min. after the moment of inserting the tubes was taken as the starting time; and at this time one tube was removed for an estimation the result of which gave the corresponding " initial " concentrations. For reactions of still lower half-change periods, a time 15 secs. after the moment of inserting the tubes was taken as the starting time, and at this moment a tube was removed, and shaken vigorously under cold water for a few seconds, for the estimation which was to provide the " initial " concentrations.

In the following tables concentrations, c, are in mols./litre, and the velocity coefficients are in the units specified on p. 240. These coefficients are defined in terms of time and concentration only, *viz.*, rate = k_2 [Cation] [Anion], and rate = k_1 [Cation], the activity factor being neglected for lack of an accurate data. The percentage of reaction is denoted by p;

Trimethylsulphonium hydroxide.

Solvent.	100% H_2O.						40% H_2O + 60% EtOH.			
Expt. No.	1		2		3		4		5	
$[Me_3S \cdot OH]_{p=0}$	0·2919		0·1607		0·1050		0·2117		0·2085	
$[NaOH]_{p=0}$	—		—		0·2464		—		0·1995	
	p.	k_2.	p.	k_2.	p.	k_2.	p.	k_2.	p.	k_2.
	12·1	0·118	17·8	0·134	11·9	0·132	8·1	5·02	14·4	4·20
	17·6	0·122	29·4	0·129	20·5	0·112	15·2	5·10	23·9	4·28
	22·8	0·120	38·1	0·127	29·7	0·117	21·4	5·15	33·0	4·33
	28·0	0·122	48·6	0·129	45·9	0·118	27·1	5·26	40·9	4·39
	34·2	0·127	56·0	0·135	53·1	0·118	31·4	5·18	47·0	4·34
	39·5	0·132	62·1	0·134	61·0	0·120	35·8	5·29	52·1	4·31
	44·1	0·131	64·2	0·135	66·8	0·118	43·6	5·48	61·4	4·36
	44·9	0·129	74·0	0·138	75·0	0·126	49·0	5·45	68·4	4·34
	53·0	0·134					53·2	5·42	73·9	4·36
	57·6	0·130					62·7	5·33	85·3	4·42
	63·6	0·133	Adopted value of k_2 for				69·5	5·40	90·8	4·42
	67·9	0·133	$c \sim 0·1, = 0·133$.				74·7	5·54	94·9	4·58
	73·2	0·134					Adopted k_2 ($c \sim 0·1$) = 5·44			
	78·6	0·146								

Solvent.	20% H_2O + 80% EtOH.		100% EtOH.		" 60% Aqueous EtOH." *			
Expt. No.	6		7		8		9	
$[Me_3S \cdot OH]_{p=0}$	0·1885		0·0590		0·00273		0·00232	
$[NaOH]_{p=0}$	—		—		—		0·00622	
	p.	k_2.	p.	k_2.	p.	k_2.	p.	k_2.
	15·6	59·1	17·6	2600	12·7	10·8	9·8	12·8
	27·5	60·5	32·4	2620	25·9	12·7	18·2	12·2
	37·1	62·0	43·5	2900	32·2	11·5	23·5	11·3
	44·9	63·5	48·2	2830	38·9	11·6	29·9	11·1
	50·1	64·0	53·7	2830	48·6	11·7	34·1	10·6
			60·1	2440	52·4	11·4		
	Adopted k_2 for		66·7	2710	67·2	12·5		
	$c \sim 0·1, = 64·0$		70·3	2420				
			Mean $k_2 = 2670$		Mean $k_2 = 11·7$		Mean $k_2 = 11·6$	

* See p. 242.

the corresponding values of k_2 or k_1 are those calculated from the above formulæ after integration for the range 0 to p.

The bimolecular character of the reaction is confirmed by the approach to equality of the products of the period of half-change and the initial concentrations, *viz.*, 7·6 and 7·7 for Expts. 1 and 2 respectively. The variation of the bimolecular coefficient with ionic strength can be seen from the values for a single run (Expts. 1, 2, 4, 6), or by comparing different runs in the same solvent (Expts. 1, 2, 3; or 4, 5); the change is in the right direction, and is of the order of magnitude to be expected for activity effects in reactions between univalent ions of unlike charge. The experiments conducted in the presence of added sodium hydroxide (Nos. 3, 5, 9) show that the reaction is of the first order with respect both to the sulphonium cation and to the anion. In Expts. 3 and 5 the ionic strength is comparatively large but buffered, and accordingly the coefficients are low but comparatively constant. Expts. 8 and 9 were carried out after the others, and with a separate sample of aqueous alcohol of approximately the composition shown (it cannot be assumed that this solvent has exactly the same composition as that used for Expts. 4 and 5). These experiments prove that the reaction remains of the first order with respect to each ion at the greatest dilutions for which accurate measurement was possible. Owing to the large dilutions, the coefficients do not drift appreciably, nor do they become changed by the addition of excess of sodium hydroxide; they should be within a few units per cent. of the constants appropriate to infinitesimal ionic strength.

Trimethylsulphonium phenoxide.

Expt. No. 10. Solvent: 100% EtOH. $[Me_3S \cdot OPh]_{p=0} = 0 \cdot 1311$. $[NaOPh]_{p=0} = 0 \cdot 0078$.

p	8·9	14·8	21·7	28·2	33·2	38·2	49·5	53·0	65·1	73·3	78·4	81·1
k_2	47·8	41·6	(32·8)	43·8	42·9	45·2	46·7	48·0	51·2	55·5	56·8	55·3

Mean k_2 $(c \sim 0 \cdot 1) = 48 \cdot 6$

Expt. No. 11. Solvent: 100% EtOH. $[Me_3S \cdot OPh]_{p=0} = 0 \cdot 0949$. $[NaOPh]_{p=0} = 0 \cdot 1610$.

p	13·7	24·5	34·9	43·6	48·6	54·0	61·8	65·0	73·3	84·2	89·9	94·0
k_2	36·0	35·0	36·4	37·1	35·0	34·5	37·6	36·2	37·6	37·0	35·2	35·6

Mean k_2 $(c \sim 0 \cdot 2) = 36 \cdot 1$

These two experiments, in one of which a substantial excess of phenoxide ions was present, show the reaction to be of the first order with respect both to the sulphonium cation and to the anion. The difference between the two mean constants is in the direction, and of the order of magnitude, to be expected from the omission of corrections for activity.

Trimethylsulphonium carbonate.

Solvent, 100% EtOH.

Expt. No.	12		13		14		15		16	
$[(Me_3S)_2CO_3]_{p=0}$	0·0362		0·0314		0·0680		0·1155		0·1712	
$[(NEt_4)_2CO_3]_{p=0}$	—		0·0287		—		0·0545		—	
	p.	k_2.	p.	k_1.	p.	k_1.	p.	k_1.	p.	k_1.
	11·7	7·3	0·250							

	p.	k_2.	k_1.	p.	k_1.	p.	k_1.	p.	k_1.	p.	k_1.
	11·7	7·3	0·250	13·4	0·266	12·5	0·267	22·1	0·250	14·1	0·303
	21·1	7·4	0·237	25·5	0·271	18·6	0·246	31·5	0·251	25·9	0·298
	30·4	8·1	0·243	35·7	0·271	32·7	0·264	39·3	0·250	36·1	0·297
	38·2	8·6	0·241	44·5	0·270	41·1	0·264	46·2	0·247	45·4	0·301
	45·2	9·2	0·242	52·1	0·272	48·0	0·261	52·5	0·248	53·1	0·302
	51·4	9·8	0·242	58·1	0·268	54·2	0·270	63·2	0·250	66·5	0·301
	61·7	11·2	0·240	69·0	(0·227)	65·0	0·263	71·1	0·248	75·0	0·308
	70·1	13·1	0·242			79·1	0·262	78·1	0·260		
	76·4	15·0	0·242			88·4	0·269	86·5	0·250		
		Mean $k_1 = 0 \cdot 242$		Mean $= 0 \cdot 270$		Mean $= 0 \cdot 263$		Mean $= 0 \cdot 250$		Mean $= 0 \cdot 301$	

In the record of Expt. 12 the bimolecular coefficient is included for comparison : the variation exposed is typical for the series. The constancy of the unimolecular coefficients, and the circumstance that they are unaltered by the addition of extraneous carbonate (Expts. 13 and 15), show the reaction to be of the first order with respect to the sulphonium ion and of zero order with respect to the anion. In contrast to the bimolecular coefficients of the previous sections, these unimolecular coefficients do not vary greatly with the ionic strength of the solution, and this is consistent with the theory of ionic strength effects on reaction velocity. The mean value of k_1 is *0·265* hr.$^{-1}$.

Trimethylsulphonium bromide.

An initial velocity only was determined :

Expt. No. 17. Solvent, 100% EtOH. $[Me_3S \cdot Br] = 0 \cdot 1047$. $k_1 = 0 \cdot 279$.

Trimethylsulphonium chloride.

Expt. No. 18. Solvent, 100% EtOH. $[Me_3S\cdot Cl]_{p-0} = 0.0480$. Mean $k_1 = 0.263$.

p	12·2	22·8	32·1	40·8	48·0	55·1	65·3	72·4	79·0
k_1	0·261	0·259	0·259	0·262	0·261	0·267	0·270	0·262	0·262

Triethylsulphonium hydroxide.

Solvent.	100% H_2O.			40% H_2O + 60% EtOH.		20% H_2O + 80% EtOH.
Expt. No.	19	20	21	22	23	24
$[Et_3S\cdot OH]_{p-0}$	0·1905	0·3619	0·2955	0·1847	0·1817	0·1535
$[NaOH]_{p-0}$	—	—	0·3600	—	0·2347	—
Range of p	11·1—65·4	18·2—79·0	16·2—74·0	10·4—75·5	33·0—98·0	14·4—49·1
Range of k_2	0·098—0·109	0·099—0·107	0·060—0·094	7·47—8·06	6·17—7·54	66·0—76·0
k_2 $(c \sim 0.1)$	Adopted (from Expt. 19) 0·101			Adopted 7·55		Mean 73·8

These results are given in summary as they are very similar to those for trimethylsulphonium hydroxide. The products of the periods of half-change and the initial concentrations for Expts. 19 and 20 are 9·9 and 10·0 respectively, in conformity with the bimolecular character of the reaction, which is also shown by the invariance of the coefficients within the limits permitted by the variations of ionic strength.

· The reaction in water proceeds to the extent of 86% in the direction of the elimination leading to ethylene, and 14% in the direction of the substitution giving ethyl alcohol (cf. Ingold and Kuriyan, J., 1933, 991). The corresponding constants ($c \sim 0.1$) are therefore k_2 (elimination) *0·087* and k_2 (substitution) *0·014*. The reactions in 60% and 80% alcohol go wholly in the direction leading to the olefin.

Methyldiisopropylsulphonium hydroxide.

Solvent.	100% H_2O.		40% H_2O + 60% EtOH.	
Expt. No.	25	26	27	28
$[MePr^\beta_2S\cdot OH]_{p-0}$	0·00290	0·00290	0·1331	0·1246
$[NaOH]_{p-0}$	—	0·00326	—	0·1257

p.	$100k_1$.	p.	$100k_1$.	p.	k_2.	p.	k_2.
6·6	0·753	7·6	0·817	13·4	6·94	34·3	6·58
15·9	0·666	13·4	0·742	26·5	(9·13)	42·8	6·66
20·8	0·776	20·1	0·767	33·4	7·48	48·6	6·45
29·4	0·798	28·6	0·772	38·0	6·90	54·4	6·43
37·3	0·912	37·2	0·910	43·0	6·77	64·2	6·44
42·4	0·757	42·3	0·757	50·4	6·52	70·1	6·17
52·5	0·795	53·5	0·815	60·1	6·74	81·0	6·04
				63·7	6·52		
				71·2	7·45		

Mean $100k_1$	*0·779*		*0·797*		74·6	6·60	Adopted k_2 (for
					77·0	6·04	$c \sim 0.1$; from Expt.
Range of k_2	2·69—6·11		1·06—1·49		81·1	6·45	No. 27) : *6·76*

Expts. Nos. 25 and 26 show that the reaction in dilute aqueous solution is unimolecular, dependent on the sulphonium cation, and independent of the anion. There is no elimination of olefin under these conditions : the reaction under observation is the substitution leading to *iso*propyl alcohol. For this reaction $k_1 = 0.00788$. Expts. 27 and 28 prove that the decomposition in 60% alcohol is bimolecular. In this case also the reaction proceeds in a single direction : it is the elimination process leading to propylene.

Methyldiisopropylsulphonium iodide.

Expt. No. 29. Solvent, 100% H_2O. $[MePr^\beta_2S\cdot I]_{p-0} = 0.04425$. Mean $k_1 = 0.00631$.

p	6·0	11·6	16·6	23·7	30·5	36·0	45·9
$100k_1$	0·626	0·604	0·601	0·650	0·640	0·635	0·634

(Range of $k_2 = 0.144—0.191$)

Expt. No. 30. Solvent, 100% H_2O. $[MePr^\beta_2S\cdot I]_{p-0} = 0.00236$. Mean $k_1 = 0.00710$.

p	7·1	13·4	19·0	27·2	34·3	40·8	50·0
$100k_1$	0·741	0·716	0·705	0·704	0·701	0·699	0·696

(Range of $k_2 = 3.26—4.25$)

The reaction is shown to be unimolecular by the approximate constancy of k_1 in contrast to the 20-fold variation of k_2 between the two experiments. The value of k_1 for the less concentrated solution approximates to that obtained for the hydroxide at a comparable dilution.

Examination of Reaction Products.—In order to supplement the data obtained by Ingold and Kuriyan (*loc. cit.*), the following determinations were made of the proportion of olefin eliminated from sulphonium hydroxides containing ethyl or *iso*propyl groups.

The sulphonium hydroxide solutions were heated in closed tubes at 100° for a sufficient time, and the tubes then broken under carbon tetrachloride in a stoppered bottle. Titration of the aqueous layer with acid yielded the extent to which reaction had occurred. The carbon tetrachloride layer was shaken with saturated mercuric chloride solution to remove sulphides, washed with water, treated with excess of standard bromine solution, and then titrated with thiosulphate in the presence of potassium iodide. The results were as follows :

Compound.	c.	Solvent.	Reaction, %.	Olefin, %.
(Et₃S)OH	0·0630	60% aq. EtOH	100	97·5, 101·5, 101·0
(MePrᵝ₂S)OH	0·0062	H₂O	50	0·0
,, ...	0·0616	60% aq. EtOH	100	98·3, 100·2

Part of the solution used for Expt. 10 (50 c.c.) was heated at 100° for 24 hours, and then distilled. No volatile ether was obtained. The crude anisole fraction weighed rather more than the theoretical (0·61 g.) ; the fraction rectified for analysis weighed 0·32 g. and had b. p. 154—155° (Found : C, 76·2 ; H, 7·4. Calc. : C, 75·6 ; H, 7·2%).

The *iso*propyl alcohol formed in the decomposition of methyldi*iso*propylsulphonium hydroxide in water was identified by oxidation in aqueous solution by means of chromic acid to acetone, which was detected by the iodoform reaction and by Tschelinzev and Nikitin's colour test (*J. Gen. Chem. Russ.*, 1933, **3**, 317), and isolated as its 2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p. 127°).

We thank the Chemical Society and Imperial Chemical Industries Limited for grants.

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55. *Mechanism of Substitution at a Saturated Carbon Atom. Part IV. A Discussion of Constitutional and Solvent Effects on the Mechanism, Kinetics, Velocity, and Orientation of Substitution.*

By EDWARD D. HUGHES and CHRISTOPHER K. INGOLD.

THE theories by which it has been attempted to interpret the mechanism of substitution reactions may be divided into two groups : (1) those which assume primary dissociation into ions or radicals and (2) those which postulate addition as an essential condition for the extrusion of the group replaced.

As regards aromatic substitution, theories of type (2) have an early origin, and their development in electronic schemes such as the following has yielded satisfactory explanation of this range of phenomena (Ingold and Ingold, J., 1926, 1313 ; Ingold, *Rec. trav. chim.*, 1929, **48**, 797). The schemes illustrated imply a classification of substitutions according to the electrical affinities of the reagents (cf. Ingold, J., 1933, 1121 ; *Chem. Reviews*, 1934, **15**, 225) :

Substitution by Nucleophilic Reagent (RY) :—
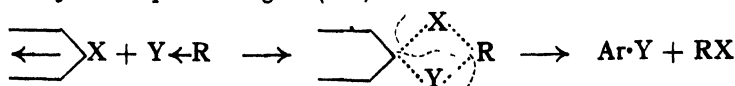
Substitution by Electrophilic Reagent (RZ) :—
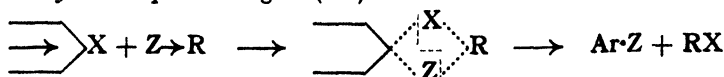
It is characteristic of these schemes that although the *orientation* of substitution is a peculiarly aromatic phenomenon, there need be nothing exclusively aromatic in the mechanism of the substitution itself (Ingold and Ingold, *loc. cit.*). It was suggested by Ingold and Rothstein (J., 1928, 1217) that even a saturated aliphatic carbon atom must be capable of forming the partial bonds of substitution complexes quite similar to those illustrated above for aromatic substitution. These authors also recognised two kinds of complex and two corresponding types of substitution depending, as before, on the electrical affinities of the reagent (cf. Ingold and Patel, *J. Indian Chem. Soc.*, 1930, **7**, 95). The formation of substitution complexes between ions and neutral molecules has been considered by Meer and Polanyi, who distinguished between substitutions brought about by positive ions and by negative ions (*Z. physikal. Chem.*, 1932, *B*, **19**, 164; cf. Bergmann, Polanyi, and Szabo, *ibid.*, 1933, *B*, **20**, 161; Olson, *J. Chem. Physics*, 1933, **1**, 418; Olson and Long, *J. Amer. Chem. Soc.*, 1934, **56**, 1294; Olson and Voge, *ibid.*, p. 1690).

All these theories belong to type (2). Olson and Voge have, indeed, objected to some existing theories of type (1) on the grounds that the assumption of primary dissociation would imply much too large a heat of activation. We use in part a form of dissociation hypothesis, and we meet this difficulty by directing attention to the important part played by solvation in ionic dissociations. The very large energy required for the formation of gaseous ions is evidently to be correlated with the circumstance that thermal ionisation does not occur in gases at relatively high temperatures. On the other hand, the spontaneity of ionisation in suitable solutions at the ordinary temperature shows that solvation must reduce both the heat of ionisation and its critical energy by an amount which is of the order of magnitude of the bond strength.

It was assumed by Ingold and Rothstein and by Ingold and Patel (*locc. cit.*) that mechanisms of both types (1) and (2) would be necessary for a complete theory of aliphatic substitution.* The first definite theory on these lines with clearly formulated consequences was advanced in Part I (Hughes, Ingold, and Patel, J., 1933, 526). This theory has been tested in considerable detail for one particular group of substitutions in Parts II and III of this series (Hughes and Ingold, J., 1933, 1571; preceding paper). It is now our object to examine from the same point of view a wider range of those aliphatic substitutions for which the necessary experimental data are available. For this purpose the fundamental considerations must be indicated in a somewhat more general form than heretofore.

The theory has reference to reactions in solution, and postulates octet-preserving electron transfers between the reagent and the seat of substitution, and between the latter and the replaced group. This assumption would not usually be true for homogeneous gas reactions for the reason given above, and there may be exceptions to the general rule even for reactions in solution. Exceptions are likely to arise in substitutions involving odd-electron reagents (*e.g.*, photochemically atomised halogens), or organic radicals in which the resonance energy is near the bond strength. We take the view, however, that special treatment should be accorded to these cases, and that the success of the electron-transfer hypothesis in the theory of aromatic substitution justifies its adoption as a basis for the general consideration of substitution at saturated carbon centres. It is an essential part of this general postulate that electron transfers may have either of two directions determined by the electronic classification of the substituting agent. According as this is nucleophilic (*e.g.*, OH′, NR_3) or electrophilic (*e.g.*, HNO_3, Cl_2), the reaction may be termed a " nucleophilic " or " electrophilic " substitution. In each case the reaction may involve the rupture of either one bond or two as shown in the formulæ below; and in each case the entering
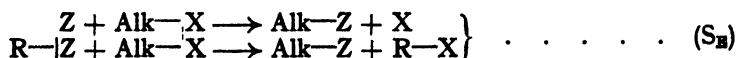
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* In Carothers and Berchet's recent discussion of the mechanism of substitutions and rearrangements (*J. Amer. Chem. Soc.*, 1933, **55**, 2809), the postulate " that $\overset{+}{R}$ is a necessary intermediate in the metathetical reactions of RX involving the formation of $\overset{-}{X}$ " should have been dissociated from the names of Ingold and his collaborators. It is to this demonstrably incorrect supposition that Carothers and Berchet's difficulties are attributable, and not, as they think, to the hypothesis (for which responsibility is accepted) that a βγ-unsaturated ion $\overset{+}{R}$, if formed, will immediately undergo balanced electronic rearrangement.—C. K. I.

B

and replaced groups may be in various states of electrification as illustrated in the preceding paper and the examples considered later.
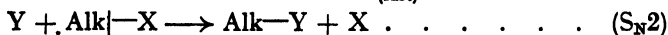
Nucleophilic Substitutions.

$$\left.\begin{array}{c} Y + Alk{-}X \longrightarrow Alk{-}Y + X \\ R{\vdash}Y + Alk{-}X \longrightarrow Alk{-}Y + R{-}X \end{array}\right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (S_N)$$

Electrophilic Substitutions.

$$\left.\begin{array}{c} Z + Alk{-}X \longrightarrow Alk{-}Z + X \\ R{-}{\vert}Z + Alk{-}X \longrightarrow Alk{-}Z + R{-}X \end{array}\right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (S_E)$$
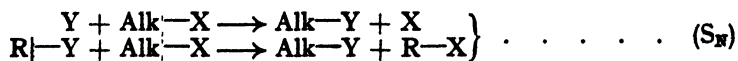
The second main postulate is that mechanisms of types (1) and (2) may operate in both categories of substitution. It is true that in the aromatic case mechanisms of type (1) never appear; but this is because the groups replaced are always held too strongly to undergo primary dissociation even in the most powerfully ionising solvents. In substitution at saturated centres, on the other hand, the more general viewpoint is required.

We envisage, in addition, the operation of steric hindrance, *i.e.*, repulsions due to the interpenetration of the atomic electron clouds at very short distances. Doubtless such effects are quantitatively important although they seldom seem to alter the direction of the broader distinctions such as those discussed in this paper.

We shall apply the theory to the deduction of constitutional effects on the kinetics and velocity of substitutions. The method has been illustrated in the preceding paper for nucleophilic substitutions; for electrophilic substitutions the method is the same in principle, although naturally many of the results are inverted. We shall also consider the deduction of solvent effects on reaction velocity. In all these aspects, attention will be directed to major distinctions of kinetics and speed; regarding small velocity differences it is recognised that there is as yet no exact theory of reaction velocity in solution.

Constitutional Effects in Nucleophilic Substitutions.

Most of the available illustrations relate to substitutions in which only one bond suffers rupture. For such reactions the two mechanisms may be formulated thus :

$$Alk{\vert}{-}X \xrightarrow[(slow)]{} \overset{+}{Alk} + X, \text{ followed by } \overset{+}{Alk} + Y \xrightarrow[(fast)]{} Alk{-}Y \quad . \quad . \quad (S_N1)$$

$$Y + Alk{\vert}{-}X \longrightarrow Alk{-}Y + X \quad . \quad . \quad . \quad . \quad . \quad (S_N2)$$

Reaction (S_N1) is unimolecular if, as is usual, the second stage is fast compared with the first, whereas reaction (S_N2) is bimolecular. Reaction (S_N1) is expected to be favoured relatively to reaction (S_N2) by the following factors : (1) large electron-release from the group Alk, (2) strong electron-affinity in the group X, (3) a sufficiently low nucleophilic activity in the reagent Y, (4) high ionising capacity in the solvent.

The substitutions to which these mechanisms may apply can be classified according to the states of electrification of the group X and reagent Y. There are four categories (*a, b, c*, and *d*, below).

(*a*) *Group X, Neutral. Reagent Y, Negative.*—Three groups of examples will be considered in relation to the replacement of a halogen atom : (i) hydrolysis, alcoholysis, etc., (ii) other substitutions by anions in reactive solvents, (iii) substitutions by anions in non-reactive solvents.

(i) We may consider first the hydrolysis of alkyl halides by means of alkali hydroxides in aqueous or alcoholic media : $OH' + Alk \cdot Hal \longrightarrow Alk \cdot OH + Hal'$.

The hydrolysis of methyl and ethyl iodides in water, methyl or ethyl alcohol, and various mixtures of these solvents, has been investigated by de Bruyn and Steger (*Rec. trav. chim.*, 1899, **18**, 41, 311), and the hydrolysis of ethyl halides in ethyl alcohol and aqueous ethyl alcohol by Grant and Hinshelwood (*J.*, 1933, 256). All these reactions are bimolecular, and the hydrolysis of ethyl iodide proceeds considerably more slowly than that of methyl iodide in an identical solvent. In the case of ethyl iodide the measured velocity was the total result of a hydrolysis giving ethyl alcohol and an elimination giving

ethylene, reactions which we regard as distinct decompositions of the halide; but even the total rate with the ethyl halide is less than with the methyl halide (*e.g.*, 1/10 for the iodides in 80% aqueous ethyl alcohol). The hydrolysis of *iso*propyl bromide by dilute solutions of alkali hydroxide in 60% aqueous ethyl alcohol has been studied by Hughes (*J. Amer. Chem. Soc.*, in the press): this reaction is unimolecular. The hydrolysis of *tert.*-butyl chloride is described in the following paper (cf. Hughes and Ingold, *Nature*, 1933, **132**, 933): this reaction is also unimolecular, and is very much more rapid than that of the *iso*propyl compound. Under the conditions chosen for the hydrolysis of the secondary and tertiary compounds there is no disturbance due to olefin elimination. The following relations are thus established for a series of groups, Alk, having progressively increasing powers of electron release:

Mechanism	S_N2		S_N1	
Group	CH_3	$CH_3{\rightarrow}CH_3$	$CH_3{\diagdown}CH_3{\diagup}CH$	$CH_3{\diagdown}CH_3{\rightarrow}C{\diagup}CH_3{\diagup}$
Reaction order	2	2	1	1
Velocity	— decrease $\longrightarrow$		— increase $\longrightarrow$	

This is exactly the type of relationship which theory predicts: it is represented in Fig. 1 of Part III.

In attempting to generalise these conclusions, it should be noted that as they stand they apply primarily to strongly ionising solvents: in less strongly ionising media the mechanistic critical point should shift towards the right, so that the *iso*propyl group and even the *tert.*-butyl group could become included in the (S_N2) category. Furthermore, owing to the great loss of intensity accompanying the relay of polar effects through saturated hydrocarbon chains, the higher primary alkyl groups are likely to fall into the same class as ethyl, the higher secondary into the same class as *iso*propyl, and so on. The velocity relation in each class can readily be deduced when the mechanistic category is known. Hence, for normal alkyl groups we expect continuously diminishing differences, provided always that, when the differences really become small, they may show disturbances from factors other than that now considered.

The hydrolysis of alkyl halides by means of alkali hydroxides in anhydrous ethyl alcohol has also been investigated by Lengfeld (*Amer. Chem. J.*, 1889, **11**, 40), Wildermann and Aisinmann (*Z. physikal. Chem.*, 1891, **8**, 661, and Anderson and Pierce (*J. Physical Chem.*, 1918, **22**, 44). The reactions with ethoxide and other alkoxides, also in dry alcohol, have been studied by Steger (*Rec. trav. chim.*, 1899, **18**, 13), Hecht, Conrad, and Brückner (*Z. physikal. Chem.*, 1889, **4**, 272), and Haywood (J., 1922, **121**, 1904; cf. Goldsworthy, J., 1926, 1102), whilst the reaction with phenoxide and other aryloxides, again in alcohol, have been examined by Conrad and Brückner (*Z. physikal. Chem.*, 1891, **7**, 274), Segaller (J., 1913, **103**, 1154, 1421; 1914, **105**, 106) and Cox (J., 1918, **113**, 666; 1920, **117**, 443). These investigations establish for all these reactions the following velocity series for the normal alkyl radicals: Me$\gg$Et$\gg$Pr$^a\gg$ higher alkyl groups, the tendency being towards a constant value as the series is ascended. In some cases it is not quite clear to what extent results are affected by olefin elimination, which, in the reaction with hydroxides, is usually more pronounced in anhydrous than in aqueous alcohol. However, Segaller states definitely that, in the reactions of the primary halides with phenoxide, olefins are not produced (his relative rates are.: Me 14·66, Et 3·03, Pr^a 1·21, Bu^a 1·15, Am^a 0·49, Hex^a 1·08, Hept^a 1·05, Oct^a 1·01, Cetyl 1·00).

The formation of olefins from halides and alkali hydroxides in anhydrous alcohol was investigated by Brussoff (*Z. physikal. Chem.*, 1900, **34**, 129), who showed that, whilst it was a minor reaction of primary halides, it was the chief mode of decomposition of secondary and tertiary halides. Most of the authors mentioned in the previous paragraph do not consider the possibility of olefin elimination, but Segaller failed to detect this in his study of the reactions between secondary halides and phenoxide. His results suggest that in the dry alcoholic solvent the secondary alkyl compounds may have passed into the (S_N2)

class, or at least reached the border line : a bimolecular formula appears to fit the results, and the velocity differences obtained for homologous secondary groups are small and somewhat irregular (all within 20% of each other from *iso*propyl to *sec.*-β-octyl iodide). On the other hand, the apparent absence of olefin elimination is rather remarkable, because in Brussoff's experiments secondary alkyl halides gave more olefins than tertiary, and Segaller observed the formation of olefins in the reactions of tertiary halides with phenoxide. Hughes's results certainly suggest that, had Segaller's solutions been more dilute (to reduce the incidence of bimolecular reactions) or the solvent more ionising, a unimolecular substitution would have been observed; and this inference is supported by the analogy of benzyl chloride, the alkaline hydrolysis and alcoholysis of which had always been described as bimolecular prior to careful investigation by Olivier (see below). Lengfeld's results also confirm the above suggestion : he measured only the percentage of reaction after a fixed time, but his values show that the hydrolyses of primary bromides are much more strongly accelerated by alkalis than are the hydrolyses of secondary bromides.

Concerning tertiary alkyl halides, both Lengfeld's and Segaller's results prove that these are much more reactive than any other simple alkyl halide. Segaller tabulated a bimolecular velocity coefficient for the phenolysis of *tert.*-butyl chloride, but the values show a marked upward drift, and a unimolecular coefficient, calculated from his data, exhibits an approximately equal downward drift. Segaller observed the formation of *iso*butylene, and the assumption that a unimolecular substitution was accompanied by a bimolecular elimination gives a satisfactory interpretation of his data.

The application of the theory to the aralphyl series, $\cdot CH_3, \cdot CH_2Ph, \cdot CHPh_2, \cdot CPh_3$, was given by Hughes, Ingold, and Patel (*loc. cit.*) : on traversing this series towards the right, there should be a point at which the mechanism changes in the sense (S_N2) $\longrightarrow$ (S_N1), after which the velocity should increase rapidly with increasing electron release.

We know that, for the reaction between halides and hydroxide ions in aqueous solvents, methyl falls into the (S_N2) class. The hydrolysis of benzyl chloride in water and aqueous acetone has recently been investigated by Olivier and Weber (*Rec. trav. chim.*, 1934, 53, 869; Olivier, *ibid.*, p. 891). This work proves that the benzyl group is *on* the (S_N2)—(S_N1) border-line : the observed kinetics corresponds to no simple type, but can be approximated as the sum of two reactions of comparable speed, one independent of the reagent hydroxide and one proportional to its concentration (we regard the real mechanism as of intermediate type). The hydrolysis of benzhydryl chloride by means of alkali hydroxide in aqueous alcohol has been studied by Ward (*J.*, 1927, 2285). This reaction proceeds in unimolecular fashion independently of the reagent hydroxide : the group $\cdot CHPh_2$ belongs definitely to the (S_N1) category.

Reference should be made to Norris and Morton's experiments on the effect of nuclear substituents on the unimolecular alcoholysis of benzhydryl chlorides (*J. Amer. Chem. Soc.*, 1928, 50, 1795), but detailed discussion may be postponed, as the discovery that secondary halides generally belong to the (S_N1) class has shown that compounds of the type Ar·CHRHal (R = Me, etc.) form an even simpler example for a study, which will be reported later, of the effects of nuclear substituents on reactions of this class.

Benzal chloride and benzotrichloride have been shown to belong to the (S_N1) class (Olivier and Weber, *loc. cit.*). Here, however, we do not emphasise the " secondary " or " tertiary " character of the halides because the mechanism of the electron-release necessary for ionisation is different : $Cl—C|—Cl$; it depends on the possession of unshared electrons by the facilitating substituent, and we think it probable that even the " primary " halide, monochloromethyl ether, will also be found to belong to the (S_N1) category : $MeO—CH_2—Cl$.

In contrast to these cases, the presence of a halogen substituent in a position other than the site of the replacement facilitates reaction by mechanism (S_N2). This may be illustrated by Tronov and Gersevic's measurements of the velocity of the reaction between sodium methoxide and some polybromoparaffins (*J. Russ. Phys. Chem. Soc.*, 1927, 59, 727) (relative rates : Pr^{a}Br, 5; Pr$^\beta$Br, 1; $CH_2Br\cdot CH_2\cdot CH_2Br$, 12; $CH_3\cdot CHBr\cdot CH_2Br$, 33;

$CH_2Br\cdot CHBr\cdot CH_2Br$, 2450). The mechanism mentioned in the previous paragraph for the electron-release which in those cases assists a primary ionisation is here unavailable, and the ordinary electron-attracting effect of halogens, which alone is now able to operate, inhibits mechanism (S_N1) and facilitates (S_N2). The effect is in direct contrast, as it should be, to that of electron-repelling alkyl substituents.

Thus the available data relating to both the kinetic type and the reaction velocity of hydrolysis and similar substitutions of alkyl halides have an unforced and unequivocal interpretation on the basis of the postulates set out above.

It is sometimes assumed that unimolecular hydrolysis is really a bimolecular reaction, occurring in a single stage, between the alkyl halide and a water molecule. However, when a water molecule does act as a direct reagent, it functions either as a base (example : hydrolysis of nitroamide), or as an acid (example : hydrolysis of acetals), or as both (example : hydrolysis of carboxylic esters), and then either the very strong base $\overset{-}{O}H$ (Brönsted's nomenclature), or the very strong acid $H_3\overset{+}{O}$, or both, as the case may be, act much more powerfully. This does not happen in the hydrolysis of *tert.*-butyl chloride, which is quite insensitive to both hydroxide and hydrogen ions. It is indeed necessary to recognise four distinct modes of action of water, which may behave (1) as solvent alone, (2) as solvent and base, (3) as solvent and acid, and (4) as solvent, base, and acid. These four modes may be distinguished experimentally by the criterion mentioned, and the hydrolysis of *tert.*-butyl chloride is found in category (1).

(ii) Two substitutions by anions in hydroxylic solvents will be referred to in this section. The first is the reaction between alkali thiosulphates and alkyl halides in water or aqueous alcohol (Slator, *J.*, 1904, **85**, 1286; 1905, **87**, 482; Slator and Twiss, *J.*, 1909, **95**, 93) : $S_2O_3'' + Alk\cdot Hal \longrightarrow Alk\cdot S_2O_3' + Hal'$. The second is that between ethyl sodioaceto-acetate and alkyl halides in absolute ethyl alcohol (Wislicenus, *Annalen*, 1882, **212**, 232) : $\overset{-}{C}HAc\cdot CO_2Et + Alk\cdot Hal \longrightarrow Alk\cdot CHAc\cdot CO_2Et + \overset{-}{H}al$.

Now it is inherent in all the reactions considered in section (i) that although, according to theory, each of the mechanisms (S_N2) and (S_N1) must exist throughout a series such as Me, Et, Pr$^\beta$, Bu$^\gamma$, only one mechanism can be observed on each side of the critical point : it is impossible to trace the broken parts of the curves in Fig. 1 of Part III. The interest of the two reactions just cited is that they are of a type for which it should be possible to trace mechanism (S_N2) into the region in which it is the minor reaction. For mechanism (S_N1), if present, would not normally be observed : the carbon cation produced by a primary ionisation would react much more often with the solvent than with the ionic reagent, and the result would be a hydrolysis or alcoholysis having only an indirect effect on the consumption of this reagent. Slator established the velocity series Me > Et > Pr$^\beta$, and Wislicenus the series Me > Et > Pr$^\beta$ > Bu$^\gamma$, the velocity for the group Bu$^\gamma$ being zero. We see here a continuous fall of velocity, as mechanism (S_N2) requires, in contrast to the passage through a minimum illustrated in the reaction of section (i).

(iii) The main example to be considered in this section is the reaction between halide ions and alkyl halides in acetone as solvent : $I' + Alk\cdot Cl \longrightarrow Alk\cdot I + Cl'$. This has been studied for a large number of simple alkyl halides by Conant and Hussey (*J. Amer. Chem. Soc.*, 1925, **47**, 475), who established the following velocity series : *primary > secondary ~ tertiary*. Concerning primary chlorides, they observed the series Et > Pr^a ~ higher primary groups, which amongst themselves showed small irregular variations (Me was not examined). Amongst homologous secondary chlorides the differences, although rather larger, exhibited no regular trend. The two tertiary chlorides examined showed only a small difference. In all cases they recorded bimolecular velocity coefficients, but their evidence that the reactions have this order, although quite definite in the case of the primary compounds, is weak for the secondary, and non-existent for the tertiary derivatives, owing to the shortness of the ranges over which the latter reactions were traced.

Our interpretation of the results is as follows. The series *primary > secondary ~ tertiary* shows indirectly that the reactions of both the primary and the secondary chlorides belong to the (S_N2) class, whilst those of the tertiary chlorides are either on the (S_N2)-

(S_N1) border-line or only just beyond it. The assumed dominance of mechanism (S_N2) in the primary series is consistent with the strong facilitating effects of electron-attracting substituents such as carbethoxy and benzoyl (Conant and Kirner, *ibid.*, 1924, **46**, 235; cf. Conant, Kirner, and Hussey, *ibid.*, 1925, **47**, 448; Bennett and Berry, J., 1927, 1676). The implied displacement of the mechanistic critical point from the position in the alkyl series in which we found it for the reactions occurring in aqueous solvents is attributed entirely to the employment in this instance of the feebly ionising solvent acetone : we think it almost certain that had the substitutions been conducted in a better ionising solvent, such as sulphur dioxide, the tertiary chlorides, and perhaps the secondary ones also, would have shown unimolecular dynamics, and the rates for the former would have been much greater than for the latter.

Lateral evidence in favour of this view is afforded by Bergmann and Polanyi's observations on the racemisation of α-chloroethylbenzene in liquid sulphur dioxide, alone and in the presence of extraneous chloride ions (*Naturwiss.*, 1933, **21**, 378). This is a reaction of the type formulated above, except that iodide ions are now replaced by chloride ions; furthermore, the alkyl group is secondary, so that the halide belongs to the general class of those which have been shown to exhibit unimolecular hydrolysis (Ward, J., 1927, 445). The racemisation in sulphur dioxide was indeed unimolecular, its speed being unaffected by the addition of the extraneous chloride ion. As a contrast, reference may be made to Bergmann, Polanyi, and Szabo's experiments (*loc. cit.*) on the racemisation of *sec.*-β-amyl and *sec.*-β-hexyl iodides by means of iodide ions in acetone : these racemisations were bimolecular, in agreement with what we have assumed concerning the reactions in this solvent of the secondary halides studied by Conant and Hussey.

(*b*) *Group X, Neutral. Reagent Y, Neutral.*—The substitutions falling within this category are those which lead to the formation of " onium " salts, *e.g.*, $NR_3 + Alk \cdot Hal \longrightarrow Alk \cdot NR_3^{\cdot} + Hal'$. The reaction between alkyl halides and triethylamine has been studied by Menschutkin (*Z. physikal. Chem.*, 1890, **5**, 589). Using acetone and benzene as solvents, he established the velocity series Me≫Et≫Pr$^\beta$ and Et>Pr$^\alpha$~higher primary groups, for which the values tended to a constant (relative rates : Me 100, Et 8·8, Pr$^\beta$ 0·18; and Et 8·8, Pr$^\alpha$ 1·7, Bu$^\alpha$ 1·2, Hept$^\alpha$ 0·9, Oct$^\alpha$ 0·9). The reactions were bimolecular. The investigation of Bu$^\gamma$ was frustrated by olefin elimination, and it is not impossible that part of the measured velocity for Pr$^\beta$ may have been due to the same cause (cf. Reboul, *Compt. rend.*, 1881, **93**, 69). The relation Me≫Et>Pr$^\alpha$ has been confirmed by Preston and Jones for the reaction of alkyl-iodides with dimethylaniline and tri*iso*amylamine in absolute ethyl alcohol (J., 1912, **101**, 1930). Having regard to the character of the solvents employed, the above results are consistent with expectation, but the reaction obviously requires investigation (and we propose to make one) in more strongly ionising solvents.

A remark may be interpolated here which applies to the reactions of both sections (*a*) and (*b*). The vinyl halides (and phenyl halides are similar) contain a *mesomeric* system $C{=}C{-}Hal$ which must strongly inhibit mechanism (S_N1) and also must oppose mechanism (S_N2), since it makes the halogen atom considerably less negative and renders the α-carbon atom more negative, although to a smaller extent. Actually, substitutions never occur by mechanism (S_N1) and only with difficulty by mechanism (S_N2). On the other hand, allyl halides (and benzyl halides are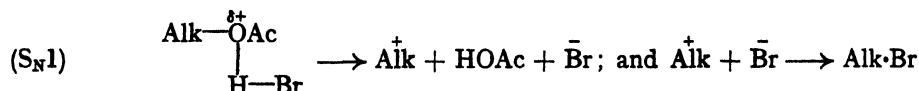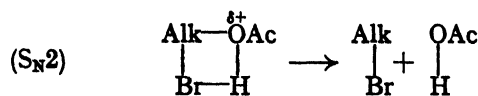 similar) have the possibility of *electromeric* polarisation of two types, one, $C{=}C{-}C{-}Hal$, which assists mechanism (S_N1), and the other, $C{=}C{\leftarrow}C{-}Hal$, which facilitates mechanism (S_N2), although to a smaller extent. Hence under *all* conditions such halides are highly reactive in nucleophilic substitutions. The literature already cited contains numerous instances of these generalisations (cf. also Juvala, *Ber.*, 1930, **63**, 1989).

(*c*) *Group X, Positive. Reagent Y, Negative.*—Substitutions of this class are encountered in the degradations of " onium salts," *e.g.*, $OH' + Alk \cdot SR_2 \longrightarrow Alk \cdot OH + SR_2$. They are the reactions by which the theory has already been illustrated in Parts I, II, and III (*locc. cit.*). Accordingly, discussion in this section will be confined to those reactions in

which the ejected group acquires its positive charge through the action of the reagent itself.

The groups ·OR and ·NR$_2$ are typically cationogenic, and their ease of separation from carbon in reactions involving electron transfers in solution is given by the sequence (F<)OR<NR$_2$. We shall express the charged modifications, the electron-attraction of which assists replacement, by the formulæ ·$\overset{+}{O}$HR and ·$\overset{+}{N}$HR$_2$, although the absence hitherto of identified Raman lines for the entity H$_3\overset{..}{O}$ suggests that this conception may have to be partly replaced by that of a formally neutral group deriving its positive charge from a protonic atmosphere.

The fission of alkyl acetates by means of hydrogen bromide in glacial acetic acid has been studied by Tronov and Sibgatullin (*Ber.*, 1929, **62**, 2850). The products are the alkyl bromide and acetic acid, and having regard to the character of the solvent and the known mechanism of the hydrolysis of esters by hydrogen ions, it seems clear that the substitution is of the type for which two links have to suffer fission. The mechanisms (S$_N$2) and (S$_N$1) must be formulated thus :

$$(\text{S}_\text{N}2) \qquad \overset{\underset{\displaystyle |}{\text{Alk}}\overset{\delta+}{-}\overset{\underset{\displaystyle |}{\text{O}}}{}\text{Ac}}{\underset{\text{Br}-\text{H}}{}} \longrightarrow \overset{\text{Alk}}{\underset{\text{Br}}{|}} + \overset{\text{OAc}}{\underset{\text{H}}{|}}$$

$$(\text{S}_\text{N}1) \qquad \overset{\text{Alk}\overset{\delta+}{-}\text{O Ac}}{\underset{\text{H}-\text{Br}}{|}} \longrightarrow \overset{+}{\text{Alk}} + \text{HOAc} + \overset{-}{\text{Br}}; \text{ and } \overset{+}{\text{Alk}} + \overset{-}{\text{Br}} \longrightarrow \text{Alk}\cdot\text{Br}$$

Tronov and Sibgatullin have established a velocity minimum in the series Me>Et~ Pr$^\beta$<<Bu$^\gamma$ (relative rates : 65, 11, 11, 2 × 10^6), and have shown that amongst primary groups the speed is decreased by increased chain length and by branching (relative rates : Et 11, Pr^a 9, Bu^a 6, Hex^a 7; *iso*amyl 5; *iso*butyl 1). Our interpretation is that methyl and primary esters use mechanism (S$_N$2) only, that secondary esters employ both mechanisms, and tertiary esters mechanism (S$_N$1) only, in their reactions with hydrogen bromide. A closely similar view may be applied to the fission of ethers by means of hydrogen bromide in acetic acid (above equations with Ac replaced by Ph, etc.), for which Tronov and Ladigina have established a minimum velocity in the series Me>Et<Pr$^\beta$<<Bu$^\gamma$, and a velocity diminishing with ascent of the primary series (*Ber.*, 1929, **62**, 2844). Yet another analogous reaction is the conversion of alcohols into alkyl chlorides by the action of hydrogen chloride in benzene (above equations with Ac replaced by H, and Br by Cl), for which Petrenko-Kritschenko, who did not examine methyl chloride, found the series *primary < secondary < tertiary* (*Z. physikal. Chem.*, 1925, **115**, 289; cf. also Norris, Watt, and Thomas, *J. Amer. Chem. Soc.*, 1916, **38**, 1071). The acid hydrolysis of acetals (Skrabal, Schiffrer, and Mirtl, *Z. physikal. Chem.*, 1921, **99**, 290; 1924, **111**, 98) provides an example of ionic fission promoted by electromeric polarisations of the type already illustrated in relation to the hydrolysis of benzal and benzotri-chloride : RO$\overset{\frown}{-}$CH$_2\overset{+}{-}\overset{+}{O}$HR.

The C–N bond is less vulnerable, and examples of its fission by a substitution reaction in amines are scarce. Kharasch and Howard, however, have shown that triphenyl-methylamine is hydrolysed by acids (*J. Amer. Chem. Soc.*, 1934, **56**, 1374), and they could not observe a similar reaction with other amines; the triphenylmethyl group is the most favourable in our alkyl series for the observation of mechanism (S$_N$1). Hickinbottom has stated that *tert.*-butylaniline is hydrolysed by aqueous acids to *tert.*-butyl alcohol (*J.*, 1934, 1702) although the reason for assuming the production of this rather than of *iso*-butylene is not clear. We should regard this hydrolysis also, if confirmed, as an exemplification of the principles developed in these papers.

(*d*) *Group X, Positive. Reagent Y, Neutral.*—Substitutions of this type, which may be illustrated by the equation NR$_3$ + Alk·$\overset{..}{S}$R$_2$ ⟶ Alk·$\overset{+}{N}$R$_3$ + SR$_2$, have not yet been discovered, but we include them for the sake of completeness, and because theory not only

shows that they must exist, but also predicts in considerable detail the kinetic phenomena with which they will be found to be associated.

The remarks at the conclusion of section (*b*) concerning allyl and similar groups apply equally to the reactions of sections (*c*) and (*d*), and numerous confirmatory examples are to be found in the literature cited in section (*c*). On the other hand, the remarks relating to vinyl and similar groups have no application in sections (*c*) and (*d*) for obvious reasons.

Solvent Effects in Nucleophilic Substitutions.

The views expressed above may readily be developed to yield a theory of solvent action which probably has considerable generality, although we shall illustrate it by reference to nucleophilic substitutions, restricting the treatment for simplicity to those substitutions in which only one bond is broken and only one is formed.

In mechanism (S_N1) the speed is determined by an ionisation, and this implies the existence of a critical energy of ionisation. A condition which would lead to such a critical energy is that, beyond a certain degree of extension of the polarised link, the increasing solvation due to the separating electric charges contributes a fall of energy which is more rapid than the rise that would have occurred in the absence of solvation; this condition satisfied, a slow ionisation results. With full recognition of the circumstance that the process of separation is continuous, the degree of extension referred to may be said to characterise a " critical complex." For a bimolecular process, such as mechanism (S_N2) implies, the conception of a critical complex is now a commonplace. It is obvious that for either mechanism the reduction of the energy of activation by a given solvent is equal to the reduction of the energy of the critical complex, *minus* the reduction of the energy of the factors (cf. Polanyi, *Z. Elektrochem.*, 1929, **35**, 561).

We now introduce the following plausible assumptions concerning the degree of solvation arising in any given solvent from the presence of electric charges : (i) solvation will increase with the magnitude of the charge; (ii) solvation will decrease with increasing distribution of a given charge. We have then only to consider the magnitude and distribution of the charges in the " critical complex " in relation to those in the factors, in order to deduce the effect of solvation on the energy of activation and the velocity; and, whatever the direction of the effect may be, its magnitude will be greater in strongly solvating (ionising) than in feebly solvating solvents.

The following table illustrates the deduction by this method of the directions of the solvent effects to be expected for the types of nucleophilic substitution considered under the headings (*a*), (*b*), and (*c*) in the previous section. Similar deductions could easily be made for the undiscovered reactions of class (*d*). We may anticipate that effects on velocity due to the dispersal in the critical complex of a given charge are likely to be less than the effects caused by the creation or disappearance of charges.

Type and mechanism.	Charges concerned in rate-determining stage of reaction.			Effect on charges of forming complex.		Expected effect of ionising media.
	Factors.	Complex.	Products.	Magnitude.	Distribn.	
1. (a) (S_N1)	RX	$\overset{\delta+}{R}\ldots\overset{\delta-}{X}$	$\overset{+}{R} + \overset{-}{X}$	Increase	—	Accelerate
2. (S_N2)	$\bar{Y} + RX$	$\overset{\delta-}{Y}\ldots R\ldots\overset{\delta-}{X}$	$YR + \overset{-}{X}$	No change	Dispersed	Retard
3. (b) (S_N1)	RX	$\overset{\delta+}{R}\ldots\overset{\delta-}{X}$	$\overset{+}{R} + \overset{-}{X}$	Increase	—	Accelerate
4. (S_N2)	$Y + RX$	$\overset{\delta+}{Y}\ldots R\ldots\overset{\delta-}{X}$	$\overset{+}{Y}R + \overset{-}{X}$	Increase	—	Accelerate
5. (c) (S_N1)	$R\overset{+}{X}$	$\overset{\delta+}{R}\ldots\overset{\delta+}{X}$	$\overset{+}{R} + X$	No change	Dispersed	Retard
6. (S_N2)	$\bar{Y} + R\overset{+}{X}$	$\overset{\delta-}{Y}\ldots R\ldots\overset{\delta+}{X}$	$YR + X$	Decrease	—	Retard

Five of these deductions can be tested by reference to the literature : all are correct. Hughes has shown (following paper) that the rate of hydrolysis of *tert.*-butyl chloride (*a*, 1) is increased on increasing the proportion of water in an aqueous alcoholic solvent. De Bruyn and Steger (*loc. cit.*) proved that the speeds of hydrolysis of methyl and ethyl iodides (*a*, 2) are decreased on increasing the proportion of water in aqueous alcohol;
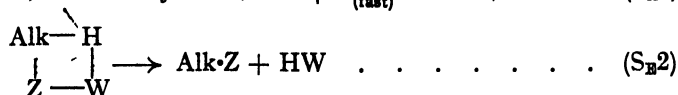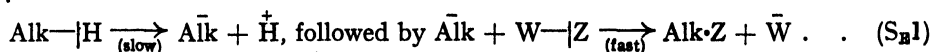
and furthermore, Bergmann, Polanyi, and Szabo (*loc. cit.*) found the rate of racemisation of secondary iodides in acetone (*a*, 2) to be decreased on addition of a small proportion of water. Menschutkin (*loc. cit.*) found the combination of ethyl iodide with triethylamine (*b*, 4) to proceed more rapidly in alcohols than in hydrocarbons (*e.g.*, MeOH > EtOH > Me_2CO > C_6H_6 > C_6H_{14}), and the same general sequence has been confirmed for other primary alkyl, or methyl, halides and other amines, or sulphides (*b*, 4), by a number of subsequent investigators (Carrera, *Gazzetta*, 1894, **24**, i, 180; Hemptinne and Bekaert, *Z. physikal. Chem.*, 1899, **28**, 225; von Halban, *ibid.*, 1913, **84**, 128; Cox, J., 1921, **119**, 142; Hawkins, J., 1922, **121**, 1170; Muchin, Ginsberg, and Moissejera, *Ukraine Chem. J.*, 1926, **2**, 136; McCombie, Scarborough, and Smith, J., 1927, 802; Essex and Gelormini, *J. Amer. Chem. Soc.*, 1926, **48**, 882). Von Halban proved (*Z. physikal. Chem.*, 1909, **67**, 29) that the decomposition of triethylsulphonium iodide (*c*, 5) takes place more slowly in alcohols than in acetone, and we have shown (Part II, *loc. cit.*) that the rate of hydrolysis of the dimethyl-*tert.*-butylsulphonium cation (*c*, 5) is decreased on increasing the proportion of water in an aqueous alcoholic solvent. Finally, we have found with Gleave (Part III) that the speed of hydrolysis of the trimethylsulphonium cation (*c*, 6) is also decreased by the same change of solvent.

Reference has already been made (cf. also Hughes, *J. Amer. Chem. Soc.*, in the press) to the possibility of changing even the order of a reaction by changing the solvent. A radical alteration such as this is likely to be realised most easily in reactions, such as those of class (*a*), in which not only the magnitude but also the direction of the solvent effect on velocity is different for the two possible mechanisms. For this group of reactions, more extensively ionising solvents should favour the change $(S_N2) \longrightarrow (S_N1)$. Very recently an alteration of this type has been observed by Olivier (*loc. cit.*), who found that the hydrolysis of benzyl chloride, which in 50% acetone is approximately bimolecular, became much more nearly unimolecular when the solvent was water alone.

Doubtless, the considerations advanced are likely to constitute the chief factor in the determination of solvent effects on reaction velocity only in reactions in which ions are produced or destroyed. A general theory of solvent effects must also envisage other factors, such as the specificity of energy exchanges between solute and solvent.

Electrophilic Substitutions.

The principal examples relate to the replacement of hydrogen in substitutions in which two bonds are broken, and for such cases the two typical mechanisms may be formulated thus :

$$\text{Alk---|H} \xrightarrow[\text{(slow)}]{} \bar{\text{Alk}} + \overset{+}{\text{H}}, \text{ followed by } \bar{\text{Alk}} + \text{W---|Z} \xrightarrow[\text{(fast)}]{} \text{Alk·Z} + \bar{\text{W}} \quad . \quad . \quad (S_E1)$$

$$\begin{array}{c} \text{Alk---H} \\ | \quad \quad | \\ \text{Z ---W} \end{array} \longrightarrow \text{Alk·Z} + \text{HW} \quad . \quad . \quad . \quad . \quad . \quad (S_E2)$$

Reaction (S_E1) will be favoured in comparison with reaction (S_E2) by (i) strong electron-attraction by the group Alk (if this contains substituents which endow it with such an effect), and (ii) strong proton affinity in the medium. The more important electrophilic reagents include nitric and sulphuric acids and the halogens.

The expected kinetic relations may be indicated. In a series such as Me, Et, Pr^β, Bu^γ, the speed of reaction by mechanism (S_E2) should progressively increase. This should be true even for the substitution of paraffin hydrocarbons; for, although the differences of permanent polarity between the carbon atoms of a paraffin must be extremely small, yet those atoms will become most negative on the approach of an electrophilic reagent which would permanently have been the most negative atoms had they been attached to a negative substituent. Thus, corresponding to Fig. 1 of Part III, a diagram could be constructed in which the curve for mechanism (S_E2) would slope upwards to the right; but in a left-ward continuation of the same diagram, extended to include the effect of reversing the polarity of alkyl groups by substitution, a point should be encountered from which another curve representing mechanism (S_E1) should slope upwards to the left.

It is well known that, in the halogenation and nitration of paraffins, tertiary hydrogen is more readily replaced than secondary, and secondary than primary. This has been established, *e.g.*, for nitration by Konowalow (*Compt. rend.*, 1892, **114**, 26; *Ber.*, 1895, **28**, 1863, *et seq.*). Markownikoff has drawn a finer distinction by showing that, in a hydrocarbon containing no tertiary hydrogen, but only methylene and methyl groups, nitration will occur at the methylene group adjacent to the most highly substituted carbon atom (*Ber.*, 1900, **33**, 1907). Markownikoff generalised these results in the statement that substitution occurs at that carbon atom which is most under the influence of other carbon atoms. This rule is well substantiated, except in relation to a group of examples considered later. It seems probable that the mechanism we assume to apply to these simple hydrocarbons [*viz.*, (S_E2)] will persist even when alkyl polarity is reversed by moderately strongly electron-attracting substituents, for Ingold and Rothstein have shown (*loc. cit.*) that bromination is inhibited by the nitroxyl group in an *o*-nitroaryl substituent. On the other hand, there is one well-authenticated case in which the electron-attraction of the substituent is sufficient to bring about substitution by mechanism (S_E1); this is the halogenation of ketones in the presence of acids (Lapworth, J., 1904, **85**, 30; Dawson, *et al.*, J., 1909, **95**, 1860, *et seq.*; Watson *et al.*, J., 1931, 3323, *et seq.*), a reaction for which we may, in agreement with Watson, ascribe the form $\cdot CR \colon \overset{+}{O}H$ to the electron-attracting complex.

Ionic Pre-dissociation and the Stereo-orientation of Substitution.

The evidence on which we have assumed a preliminary ionisation in mechanism (S_N1) may be summarised as follows : (1) the rate of substitution is governed by a preliminary slow change in the compound substituted; (2) this preliminary change is not accelerated by bases or acids as such; (3) its rate is affected by constitution in the manner expected for ionisation; (4) its rate also shows the expected type of dependence on the solvent.

None of these consideration implies the necessity for assuming that both the ions have a long life, or even that they attain " complete " dissociation. A lower limit to the life of the carbon cation is given in some cases by the observation of complete, or almost ·complete, racemisation accompanying substitution by mechanism (S_N1). This has been observed, *e.g.*, by McKenzie and Clough for the hydrolysis of α-chloroethylbenzene and of α-chloro-α-phenylpropionic acid (J., 1913, **103**, 687; 1910, **97**, 1017); and Ward has proved that the reaction of the former compound is unimolecular (*loc. cit.*), whilst Senter and Martin have established the same point for the bromo-analogue of the latter (J., 1917, **111**, 447). Doubtless, complete racemisation would be the rule in ionising, but chemically inactive, solvents such as sulphur dioxide. On the other hand, there are substitutions of type (S_N1) in which perceptible optical activity persists in the product, and this shows that decomposition of a water molecule by the cation may occur rather soon after the ionisation has passed over its energy barrier. The reaction might then be described as depending on ionic pre-dissociation.

Mechanism (S_E1) is in a similar case. An appreciable retention of optical activity during the bromination of 2-*o*-carboxybenzylindanone has been reported (Leuchs, *Ber.*, 1913, **46**, 2435; cf. *ibid.*, 1915, **48**, 1015), but the reaction was conducted in a non-ionising solvent and the kinetics obtaining under these conditions are unknown. It has, however, been shown that, when this ketone is brominated in aqueous acetic acid in the presence of a strong acid, the kinetics of the reaction correspond to mechanism (S_E1) and racemisation is complete (Ingold and Wilson, J., 1934, 773).[*]

When complete racemisation does not occur during a substitution, the question of the configuration of the product arises. Polanyi has suggested that inversion always accompanies substitutions by negative ionic reagents, and Olson has advanced the view that inversion is a concomitant of one-stage substitutions generally (*locc. cit.*). We think that different substitution mechanisms should be considered independently in this connexion,

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[*] This follows from the recorded comparison of the rates of racemisation and bromination. These authors directly verified the optical inactivity of the bromo-ketone by isolating it, but, owing to an oversight, omitted to mention this observation in their paper.

and may tentatively indicate a third possibility, *viz.*, that inversion is the rule for mechanisms (S_N2) and (S_E2), whilst retention of configuration may occur in (S_N1) and (S_E1).

This question will later be discussed in its relation to the unimolecular substitutions. With regard to the bimolecular substitutions, it may be noted that the experimental evidence of inversion adduced by Polanyi and Olson applies primarily to mechanism (S_N2). Indirect evidence that inversion is also general for mechanism (S_E2) may be seen in the fact that the orientation rules for electrophilic substitutions in aliphatic compounds break down completely when applied to rigid polycyclic systems such as the camphane structure. This contains a tertiary hydrogen atom; yet there is no established instance of substitution in this position, which remains unattacked whilst halogenations, nitrations, and sulphonations occur in the methylene and even in the methyl groups of camphane derivatives. Obviously, this should be so if substitution requires inversion; for inversion in the tertiary position would necessitate a simultaneous inversion at the other bridge-head, for which there is no mechanism.

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56. *Mechanism of Substitution at a Saturated Carbon Atom. Part V. Hydrolysis of tert.-Butyl Chloride.*

By EDWARD D. HUGHES.

THE nucleophilic substitution theory of Hughes, Ingold, and Patel (J., 1933, 526) was, in the first instance, applied to the fission of organic cations, but, as predicted at the time, it can be equally successful in explaining the analogous reactions of neutral molecules. One of the substitutions referred to in this connexion was the hydrolysis of alkyl halides : OH' + Alk·Hal ⟶ Alk·OH + Hal'. In its application to this reaction the theory recognised a bimolecular mechanism involving the attack of the carbon–halogen link by hydroxide ions, and also a unimolecular mechanism kinetically dependent on the ionisation of the alkyl halide. It was anticipated that there would be a change over from the bimolecular to the unimolecular mechanism towards the right-hand end of a series of alkyl halides arranged in order of increasing electron-release of the alkyl groups; *e.g.*, as shown in Series i of Part III. It was also expected that, from the left of such a series, where the bimolecular mechanism takes control, to the point at which the mechanism changes, the absolute velocity of the reactions of corresponding halides (*e.g.*, chlorides) should decrease; and that, from the point at which the unimolecular mechanism becomes dominant, towards the right, the absolute velocity should increase.

It is known (preceding paper) that the hydrolysis of methyl and ethyl halides is bimolecular, and that the reactions of the ethyl halides are slower than those of the methyl halides. It is also known that *iso*propyl halides are hydrolysed slowly (Part IV, preceding paper), whilst *tert.*-butyl halides are hydrolysed rapidly (Butlerow, *Annalen*, 1869, **144**, 33; Dobbin, J., 1880, **37**, 237; Strauss, *Annalen*, 1909, **370**, 366; Michael and Leupold, *ibid.*, 1911, **379**, 263). The existing evidence is therefore consistent with the theory, provided that there really be a change of mechanism somewhere between the ethyl and the *tert.*-butyl group. The author has now proved that the anticipated change of kinetic type occurs : the hydrolysis of *tert.*-butyl chloride is unimolecular.

This hydrolysis is therefore a reaction of the type labelled (S_N1) in the previous paper : the measured rate is the rate of ionisation of the halide. The opportunity has been taken to measure the critical energy (Arrhenius) of the reaction : the critical energy of an ionisation has thus been determined.

tert.-Butyl chloride is but sparingly soluble in water, and the kinetics were therefore studied in aqueous alcohol and aqueous acetone. The usual tests relating to reaction order were applied, thus establishing the unimolecular nature of the hydrolysis. Experiments have been carried out in aqueous media of diverse composition, and in three solvents measurements were performed at different temperatures.

A clear indication of the unimolecular nature of the reaction is obtained in experiments in which *tert.*-butyl chloride was taken in such large excess that its concentration did not appreciably change during the reaction. The velocity in dilute alkaline solution was then constant and independent of the concentration of the alkali; furthermore, when all the alkali was neutralised by the halogen acid formed, the reaction continued with the same velocity in the acid solution. This is shown in Table I, the first three columns of which are self-explanatory; col. 4 gives the average fall in titre per hour in alkaline solution, and col. 5 the average rise in titre for the same period in acid solution. The figures in both these columns relate to 10 c.c. of the reaction mixture and are expressed in c.c. of $0.05N$-acid and -alkali. The temperature was $25.0°$.

TABLE I.

Mols. halide per mol. KOH.	Solvent : Aq. EtOH EtOH, % by vol.	Range of readings : alkali $\longrightarrow$ acid (in normality).	Speed in alkaline solution.	Speed in acid solution.
61	80	$0.045 \longrightarrow 0.040$	4.96	4.92'
57	90	$0.048 \longrightarrow 0.060$	2.05	2.01

In the presence of a slight excess of potassium hydroxide, the velocity is independent of the concentration of the alkali and a good unimolecular constant is obtained. Under identical conditions of medium and temperature, the same constant is obtained in the complete absence of alkali, *i.e.*, in a solution which, as the reaction progresses, becomes more and more acidic. This is illustrated in Expts. 1 and 2 of Table II. The medium was 70% alcohol, the temperature $25.0°$.

TABLE II.

Expt. No.	1.	2.	3.	4.	5.
[Halide], M	0.0510	0.0465	0.0824	0.1322	0.1746
[KOH], N	0.0571	—	—	—	—
k_1 (hr.$^{-1}$)	0.145	0.147	0.145	0.141	0.137

In dilute solutions the velocity constant is, within the limits of experimental error, independent of the initial concentration of the alkyl halide; but, at the higher concentrations, its value shows a decided decrease. The concentration employed in Expt. 5 (Table II), where the effect is most marked, corresponds to 2 c.c. of *tert.*-butyl chloride in 100 c.c. of the reaction mixture, and as the reaction is particularly sensitive to changes in the medium, the decrease in the velocity constant is undoubtedly to be attributed to an effect of medium.

More detailed reference may now be made to the effect of medium on the reaction. The result of regularly increasing the proportion of water in an aqueous-alcoholic solvent is to cause a very marked increase in speed, as shown below (temperature = $25.0°$) :

EtOH, % by vol.	90	80	70	60	50	40
[Halide], M	0.0755	0.0762	0.0824	0.0735	0.0810	0.0306
k_1 (hr.$^{-1}$)	0.00616	0.0329	0.145	0.453	1.32	4.66

This is consistent with our views regarding the mechanism of the reaction, *viz.*, that the speed is governed by the ionisation of the halide. It is in marked contrast to the effect of replacing alcohol by water in the hydrolysis of primary alkyl halides and in the decomposition of the dimethyl-*tert.*-butylsulphonium cation (cf. Part IV).

The variation of the velocity constant, in 80% alcohol, with temperature is shown in the following table :

Temp.	8.0°	16.0°	25.0°	35.0°	45.0°
$k_1 \times 10^3$ (hr.$^{-1}$), obs.	3.12	9.76	32.9	117	374
„ „ calc.	3.10	9.71	32.9	117.5	380

In accordance with the Arrhenius equation, $k = Be^{-E/RT}$, the plot of log k_1 against $1/T$ is linear, giving an energy of activation $E = 23,060$ cals.; and the constants are in good agreement with the equation $\log_e k_1 = 35.56 - 23,060/RT$. Similar results were obtained in 50% alcohol. The plot of log k_1 against $1/T$ is again linear, $\log_e k_1 = 39.03 - 22,920/RT$, giving $E = 22,920$ cals. :

Temp.	....	8·0°	16·0°	25·0°
k_1 (hr.⁻¹), obs.	....	0·127	0·397	1·32
,, calc.	....	0·127	0·397	1·32

The velocity constants in 80% acetone are $k_{35°} = 2·39 \times 10^{-3}$ and $k_{45°} = 7·63 \times 10^{-3}$ (hr.⁻¹), giving an energy of activation of 22,600, and the general expression $\log_e k_1 = 33·23 - 22,600/RT$.

It will be observed that, although the velocity constant is decreased 40-fold in passing from 50% alcohol to 80% alcohol, and 200-fold in passing from the former medium to 80% acetone, the value of E varies but slightly in the examples studied. The variation is almost entirely accounted for in the $\log_e B$ term. Discussion is postponed pending the results of further experiments.

Experiments will be reported later showing the effect of alkyl substitution and of halogen replacement on the critical energy of ionisation, and the attempt is being made to trace its dependence on the carbon–halogen bond energies through study of unimolecular hydrolyses analogous to the one herein discussed.

EXPERIMENTAL.

tert.-Butyl chloride, prepared by Norris's method (*Amer. Chem. J.*, 1907, **38**, 641), was carefully fractionated, and the fraction of constant b. p. 50·9°/762 mm. was used.

Hydrolysis of tert.-Butyl Chloride in Water.—Butlerow's experiments (*loc. cit.*) on the production of *tert.*-butyl alcohol were confirmed. Interaction was effected by shaking for 24 hours at room temperature. The solution was then neutralised with sodium carbonate, the alcohol salted out with sodium chloride, separated, dried over anhydrous sodium carbonate, and distilled. A product, b. p. 82·5°, was obtained in good yield. It was freed from traces of water by further distillation, first from fused barium oxide, and then from dissolved sodium, and was finally obtained as a white hygroscopic solid, m. p. 25°, identified by comparison with an authentic specimen. It is important to note that no olefin could be detected under the conditions of the kinetic experiments.

Kinetic Measurements.—*Purification and preparation of media.* Ethyl alcohol was lime-dried and fractionated. Acetone was purified by the sodium iodide method (Shipsey and Werner, J., 1913, **103**, 1255), dried over calcium chloride, and fractionated. The aqueous media were made up from the pure components by volume. Any possible errors introduced in making up the solutions were eliminated in the comparative experiments by keeping a good stock and drawing from the same sample.

Methods. In the first experiments, weighed amounts of *tert.*-butyl chloride were dissolved in the appropriate medium in a well-stoppered standard measuring flask, and diluted to the mark at the temperature of the thermostat. This procedure has the disadvantage that considerable time elapses, and, in some experiments, considerable reaction takes place, before measurements can be taken. Experience showed that the production of hydrogen chloride was quantitative. In some cases, therefore, the weighing was omitted altogether, and the method was simply to dissolve an approximately measured volume of the chloride in the medium, both being at the working temperature before admixture. The concentration at any time can then be deduced from the value of the titre at that time compared with that at infinite time. 5 C.c. were usually withdrawn, and the reaction was stopped by running it into alcohol, a standardised procedure being adopted to minimise indicator errors. The residual alkali (in the experiments in alkaline solution) was titrated with standard acid, and the hydrochloric acid (in the experiments in initially neutral solution) with standard alkali. Lacmoid was used as indicator.

The following selections of detailed experiments will serve to illustrate the nature of the results from which the foregoing constants have been taken. Except where otherwise specified, t is the time in hrs., x or $a - x$ the titre of 5 c.c. of the solution expressed in c.c. of $N/40$-alkali or -acid respectively, and k_1 the unimolecular velocity constant in hrs.⁻¹.

Temp. 25·0°. Medium 70% EtOH.

(a) [Chloride] = 0·0510N, [KOH] = 0·0510N.   (b) [Chloride] = 0·0465N, [KOH] = 0.

t.	$a - x$.	10^3k_1.	t.	$a - x$.	10^3k_1.	t.	x.	10^3k_1.	t.	x.	10^3k_1.
0·5	9·48	146	4·0	5·70	145	0·5	0·65	145	4·0	4·18	149
1·0	8·83	144	5·0	4·92	146	1·0	1·28	148	5·0	4·88	149
1·5	8·23	143	6·0	4·28	145	1·5	1·85	148	6·5	5·70	146
2·0	7·63	145	8·0	3·13	147	2·0	2·38	148	8·0	6·40	146
3·0	6·63	143	10·0	2·30	149	3·0	3·32	147	10·0	7·22	149

<div align="center">Temp. 25·0°.</div>

Medium 80% EtOH; [Halide] = 0·0761N.						Medium 50% EtOH; [Halide] = 0·0810N.					
t.	x.	$10^4 k_1$.	t.	x.	$10^4 k_1$.	t (min.).	x.	$10^2 k_1$.	t (min.).	x.	$10^2 k_1$.
4·0	1·87	328	29·5	9·45	328	10	3·20	132	50	10·60	132
8·5	3·72	329	37·0	10·77	332	20	5·75	131	70	12·72	132
12·0	5·00	332	48·5	12·12	327	30	7·86	133	90	13·95	131
23·0	8·12	331	60·5	13·12	327	40	9·38	130			

Temp. 8·0°, Medium 80% EtOH. [Halide] = 0·0939N.						Temp. 35·0°, Medium 80% Acetone. [Halide] = 0·0600N.					
t.	x.	$10^4 k_1$.	t.	x.	$10^5 k_1$.	t.	x.	$10^4 k_1$.	t.	x.	$10^4 k_1$.
35·5	1·98	311	193·5	8·50	311	7	1·85	239	48	8·20	239
73·5	3·82	310	276·5	10·88	313	15	3·60	237	80	10·30	244
126·5	6·08	309	349·5	12·58	317	30	6·10	236			

The author is deeply indebted to Professor C. K. Ingold, F.R.S., for his invaluable help and encouragement.

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57. *Investigations of the Olefinic Acids. Part XVI. Additive Reactions and Tautomeric Changes of Cyclic Unsaturated Acids, and Analogous Observations on α-Methylpentenoic Acids.*

<div align="center">By E. J. BOORMAN and R. P. LINSTEAD.</div>

PREVIOUS work (J., 1932, 115; 1933, 580) has shown that the introduction of alkyl groups on the γ-carbon atom greatly increases the readiness with which Δ^β-unsaturated acids form γ-lactones, because it promotes polarisation of the double bond in the sense

$$\overset{\delta+}{Me_2C}{=}CH{\cdot}CH_2{\cdot}\overset{\delta-}{CO_2}H \longrightarrow Me_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CO$$
$$\underset{\text{O}}{\vert\underline{\qquad\qquad}\vert}$$
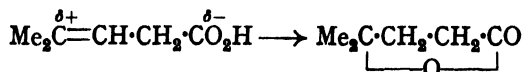
and possibly because it induces coiling of the chain. In order to assess the relative importance of these two factors we have now studied the effect of γ-alkylation on the ease of lactonisation of some cyclic Δ^β-acids, in which the molecule is more rigid and the polar effect of the γ-alkyl group will be the same as that in the open-chain series but its effect (if any) on the coiling of the molecule must be diminished. For this purpose Δ^2-*cyclo*hexenecarboxylic (tetrahydrobenzoic) acid and 3-methyl-Δ^2-*cyclo*hexenecarboxylic acid (I and II) have been examined. The configurational changes in these acids are confined to the rotation of the carboxyl group about the bond connecting it to the ring and (possibly) to the oscillation of the ring between the two Sachse (C and Z) forms, and even in the most favoured arrangement an oxygen atom of the carboxyl group cannot approach the γ-carbon atom as closely as is possible in open-chain olefinic acids.

We have also carried out a parallel examination of the tautomeric changes between these Δ^2-acids and their Δ^1-isomerides, and of their reaction with hydrogen bromide.

The preparation of the unmethylated acid (I) and its Δ^1-isomeride (III) (p. 261) presented no special features. The homologous 3-methyl acids (II and IV), previously prepared by Perkin and Tattersall (J., 1905, 87, 1085; 1907, 91, 496), were obtained in the present work by the hydrolysis of the unsaturated nitrile resulting from dehydration of the cyanohydrin of 3-methyl*cyclo*hexanone. This yielded an easily separable mixture of the Δ^1- and the Δ^6-acid (IV and V). The Δ^2-acid was prepared by equilibrating the Δ^1-acid with alkali and was purified by partial esterification. It is conceivable that the Δ^1-acid might isomerise to the Δ^6-acid under these conditions and this in turn might yield the corresponding Δ^β-acid (the Δ^5-acid, VI), which would contaminate the Δ^2-acid. It was found, however, that Δ^1-tetrahydrobenzoic acid showed little or no tendency to pass into the Δ^2-form (see p. 263), and this suggested that the Δ^6-acid of the methylated series (which has a similar

3-carbon system) would also show very little tendency to yield its Δ^β-isomeride. The 3-methyl group, on the other hand, would be expected to promote the formation of the Δ^2-double bond. Hence, even if the Δ^1-acid yielded some Δ^6-acid on equilibration, the Δ^β-acid formed was expected to be almost entirely the Δ^2-isomeride. This was justified experimentally; the isolated Δ^β-acid after careful purification by partial esterification was the Δ^2-isomeride practically free from isomeric impurity.

$$\text{(III.)} \qquad \text{(I.)} \qquad \text{(VII.)}$$

$$\text{(IV.)} \qquad \text{(V.)} \qquad \text{(VI.)} \qquad \text{(II.)} \qquad \text{(VIII.)}$$
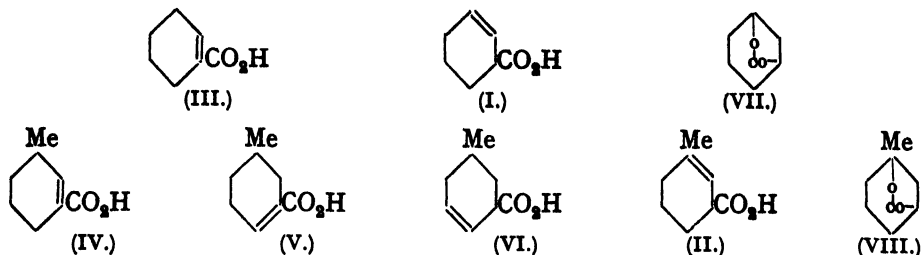
Lactonisation of the Unsaturated Acids.—Δ^2-Tetrahydrobenzoic acid (I) yielded the corresponding γ-lactone on treatment with sulphuric acid with approximately the same facility as Δ^β-hexenoic and -pentenoic acids, and did not lactonise at the b. p. The lactone was identical with the *cis*-1 : 3-*cyclo*hexanolide (VII) of Perkin and Tattersall (*loc. cit.*), which was independently synthesised for comparison. The only abnormality was the instability of the materials to sulphuric acid, the lactone being destroyed by the hot acid and the Δ^β-acid being partly polymerised in the cold.

3-Methyl-Δ^2-*cyclo*hexenecarboxylic acid (II), on the other hand, showed the expected resemblance to pyroterebic acid. On treatment with cold sulphuric acid it passed very rapidly indeed into 1-methyl-1 : 3-*cyclo*hexanolide (VIII), identical with material prepared by Perkin and Tattersall's method. The lactonisation appeared to be slightly slower than that of pyroterebic acid. Both lactone and acid were unstable to boiling dilute sulphuric acid. 3-Methyl-Δ^2-*cyclo*hexenecarboxylic acid, like pyroterebic acid, yields the corresponding lactone when boiled alone, but here the formation of lactone is *reversible*. The equilibrium, at about 33% of lactone and 67% of unsaturated acid, was approached from both sides and the system thus provides an example of ring chain tautomerism (lacto-enoic) similar to that occurring between Δ^γ-*iso*heptenoic acid and δ-*iso*heptolactone (Linstead and Rydon, J., 1933, 580). The formation of an isomeric unsaturated acid by the boiling of a γ-lactone is unique. The tautomeric change does not, however, appear to be simple, as the Δ^2-acid formed by boiling the γ-lactone appears to be contaminated with an isomeride, possibly the Δ^3-acid.

The fission of these tertiary lactones into unsaturated acids by the action of heat presents an interesting analogy with Menschutkin's demonstration that the acetates of tertiary alcohols decompose above 100° into acetic acid and an olefin (*Ber.*, 1882, **15**, 2512). Both reactions involve the migration of a hydrogen atom and the fission of a C—O link, but Menschutkin's reaction leads to the disruption of the molecule, and ours only to its rearrangement. The two processes may be represented as follows :
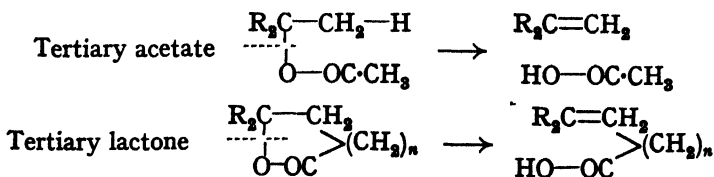
A comparison of the results obtained with the methylated and the unmethylated acids supports the view that the activity (polarisability) of the double bond is the major factor affecting the ease of lactonisation of an unsaturated acid, providing that suitable approach of the reacting centres is possible in one phase of the molecule.

Addition of Hydrogen Bromide.—This was examined in polar solvents (acetic acid, water). The orientation of the additions was determined quantitatively by methods which were standardised with pure β- and γ-bromo-acids. Owing to the proximity of the double bond to the carboxyl group, the effect of peroxides was neglected (compare Linstead and Rydon, J., 1934, 2001). The observed additions obeyed the Markownikoff rule. Thus, Δ^1-tetrahydrobenzoic acid yielded exclusively 2-bromo*cyclo*hexanecarboxylic acid (probably *trans*-), and Δ^2-tetrahydrobenzoic acid yielded 18% of this acid and 82% of the 3-bromoisomeride, which was isolated in both *cis*- and *trans*-forms. 3-Methyl-Δ^2-*cyclo*-hexenecarboxylic acid, on the other hand, gave exclusively " distant " addition of bromine, the product being 3-*bromo*-3-*methyl*cyclo*hexanecarboxylic acid*. This was mainly the *cis*-isomeride, as it readily yielded 1-methyl-1 : 3-*cyclo*hexanolide (VIII). 3-Methyl-Δ^1-*cyclo*-hexenecarboxylic acid yielded the isomeric 2-*bromo*-3-*methyl*cyclo*hexanecarboxylic acid*. These results are similar to those obtained for pentenoic and γ-methylpentenoic acids (Boorman, Linstead, and Rydon, J., 1933, 568) and indicate that the ring has no specific influence on the orientation. Ethyl 2-bromo*cyclo*hexanecarboxylate readily lost hydrogen bromide when treated with ethyl sodiomalonate to yield ethyl Δ^1-tetrahydrobenzoate (compare Cocker, Lapworth, and Peters, J., 1931, 1383; Cook and Linstead, J., 1934, 956), but the esters of the isomeric 3-bromo-acids were unaffected by the same treatment. Ethyl Δ^1-tetrahydrobenzoate added ethyl sodiomalonate (Helfer, *Helv. Chim. Acta*, 1926, 9, 816), and the product on hydrolysis gave the important *cyclo*hexane-1-carboxylic-2-acetic acid of Windaus, Hückel, and Reverey (*Ber.*, 1923, 56, 91), which was obtained as the pure *trans*-modification (compare Sircar, J., 1927, 1255).

Tautomeric Changes.—The mobility of the interconversion of both pairs of Δ^1- and Δ^2-acids in alkali was extremely low, as is often the case for more complex α-alkylated acids. The positions of equilibrium were of considerable interest, for in each case the proportion of the Δ^α-form was higher than that anticipated from a study of the analogous acyclic acids, as the following figures show :

> Tetrahydrobenzoic acids : 95·5% Δ^α-acid at equilibrium.
> α-Methylpentenoic acid : 89% Δ^α-acid at equilibrium (see p. 267).
> 3-Methyl*cyclo*hexenecarboxylic acids : 75% Δ^α-acid at equilibrium.

The γ-methyl group stabilises the Δ^β-phase to some extent in the usual manner, but no analogous open-chain unsaturated acid carrying one α- and two γ-groups is available to complete the comparison. Owing to the slowness of the tautomeric change neither of the Δ^1-acids gave an appreciable amount of lactone on treatment with sulphuric acid.

Properties of the Lactones.—When heated with water at 100°, 1 : 3-*cyclo*hexanolide (VII) yielded an equilibrium mixture containing 88% of the corresponding γ-hydroxy-acid. This is an altogether exceptional degree of hydrolysis for a γ-lactone : most members of the class yield less than 10% of hydroxy-acid under these conditions and the highest figure on record is the 25% hydrolysis of γ-butyrolactone (Boorman and Linstead, J., 1933, 580). Nevertheless the lactone undoubtedly belongs to the γ-series from the method of synthesis. Tetrahedral models indicate that the molecule is in a state of strain which can be relieved by the fission of the lactone ring, and it appears very probable that this accounts for the instability. The corresponding 3-methyl lactone (VIII) yields an equilibrium amount of 28% of hydroxy-acid. Here the tendency to fission caused by strain is opposed by the presence of the γ-alkyl group, which has been shown to stabilise monocyclic lactones by Hjelt (*Ber.*, 1896, 29, 1855) and in earlier papers of this series (compare, for example, the stability of γ-butyrolactone and γ-*iso*hexolactone).

Although the *extent* to which 3-methyl-1 : 3-*cyclo*hexanolide is hydrolysed is unusual, the *velocity* with which it is formed from its hydroxy-acid is quite normal for a γ-lactone and distinguishes it sharply from the lactones of the δ-series.

α-Methylpentenoic Acids and α-Methyl-γ-valerolactone.—The cyclic acids considered above contain in effect a chain branched at the α-carbon atom. No acyclic acids of this type have been studied under similar conditions and in view of this a control examination was made of a typical α-alkylated system—the α-methylpentenoic acids. The experiments

showed that the α-alkyl group had no marked effect on the ease of lactonisation of Δ^β-unsaturated acids. The tautomeric change between Δ^α- and Δ^β-α-methylpentenoic acid has been shown by Goldberg and Linstead to be of normal mobility (J., 1928, 2343). In support of this it was found that the Δ^α-acid yielded γ-lactone when boiled with dilute sulphuric acid. The lactone was identical with that prepared directly from the Δ^β-acid, and that of Blaise and Luttringer (*Bull. Soc. chim.*, 1905, **33**, 828). The Δ^β-acid was not lactonised when boiled alone.

It was of particular interest that α-methyl-γ-valerolactone was stable to boiling water, being hydrolysed to only 2%. It was rapidly formed from the corresponding hydroxy-acid and in these respects bore a general resemblance to the isomeric γ-methyl-γ-valerolactone (*iso*hexolactone). The fact that an α-alkyl group stabilises the γ-lactone ring confirms the view that the instability of the dicyclic lactones studied above is due to strain.

<center>EXPERIMENTAL.</center>

General Methods.—The lactonisation of unsaturated acids and the analysis and separation of the mixtures obtained were carried out by the methods described in J., 1932, 121; bromine additions (*B*) to unsaturated acids by the method of Linstead and Noble (J., 1934, 617), a reaction period of 5 minutes being used; and iodine additions (*J*) by Linstead and May's process (J., 1927, 2565). Recorded densities and refractivities are for $d_4^{20°}$ and $n_D^{20°}$ respectively.

<center>1. *Tetrahydrobenzoic Acids.*</center>

Preparation of the Δ^1-*Acid* (III).—Δ^1-Tetrahydrobenzonitrile (Ruzicka and Brügger, *Helv. Chim. Acta*, 1926, **9**, 399) was boiled for 17 hours with 10% caustic potash solution (2 equivs.); the product was treated with a slight excess of sulphuric acid and distilled in steam, 9 l. of water being required for the product from 100 g. of nitrile. The distillate was neutralised, evaporated, and extracted with ether to remove neutral and basic impurities. Acidification and extraction with ether then yielded the acid, which, after distillation (b. p. 107°/3 mm ; 138°/14 mm.), partly solidified (yield, 94 g.; 79%) (Equiv.: found, 126·8; calc., 126·1). The solid acid was collected and drained on a porous tile (m. p. 35·5°). The various products reacted with bromine as follows : semi-solid mixture, *B* 21·3%; solid acid (*a*), *B* 13·2%; liquid drainings (*b*), *B* 31·2%. This indicated that the crude acid contained about 20% of the Δ^2-isomeride.

The solid acid (*a*) was partly esterified by treatment with *N*-alcoholic hydrogen chloride (1 vol) and absolute alcohol (2 vols.) for 3 hours at room temperature and 30 minutes on the steam-bath, and the product separated into acid and ester (Eccott and Linstead, J., 1929, 2153). Pure Δ^1-tetrahydrobenzoic acid was obtained from the acid fraction after distillation as large overlapping plates, m. p. 38° (Found : C, 66·5; H, 7·9; equiv. 126·1, *B* 1·8%. Calc. : C, 66·6; H, 8·0%; equiv., 126·1). Einhorn's preparation from benzoic acid had m. p. 29° (*Ber.*, 1900, **33**, 3455). The liquid acid (*b*) was partly esterified similarly, but for 8 hours in the cold and 1 hour on the steam-bath to ensure the esterification of all the Δ^2-acid. The unesterified acid was the pure Δ^1-isomeride (equiv. 126·1, *B* 1·7%). The combined esters were hydrolysed by cold alkali, and the crude Δ^2-acid isolated by the method described for Δ^β-*iso*hexenoic acid (Linstead, J., 1932, 125). After distillation it was converted into the dibromide, m. p. 167·5° alone or admixed with the derivative of the Δ^3-acid described below.

Ethyl Δ^1-tetrahydrobenzoate, prepared by means of the silver salt, had b. p. 96°/16 mm., *n* 1·4700, *d* 0·9999, [R_L]$_D$ 42·98 (calc., 42·63). An equimolecular mixture of this and ethyl sodio-malonate was left for 3 days in the cold and heated on the steam-bath for 12 hours. The tricarboxylic ester (Helfer, *loc. cit.*) was isolated in 45% yield, b. p. 176—185°/9 mm. (This experiment was carried out before Cook and Linstead, *loc. cit.*, had shown that the corresponding condensation in the *cyclo*pentane series was best effected quickly; the yield could probably be considerably improved.) Hydrolysis with concentrated hydrochloric acid (2 vols.; 28 hours at the b. p.) yielded 92% of pure *trans*-hexahydrohomophthalic acid, m. p. and mixed m. p. 158°, equiv. 93·0 (calc., 93·05).

Preparation of the Δ^2-*Acid* (I).—Aschan's method (*Annalen*, 1892, **271**, 234) gave poor results and the reduced material was always mainly the Δ^1-acid. The following modification gave repeatedly good yields : a solution of 15 g. of benzoic acid in 75 c.c. of aqueous caustic soda was heated (steam-bath) under an air condenser, carbon dioxide passed into the liquid, and 150 g. of 5% sodium amalgam (pea size) added. After 5 hours the mercury was removed and

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50 c.c. of water and another 150 g. of amalgam were added. The process was repeated three more times, and the solution then cooled and acidified with 50% sulphuric acid. Ether extraction removed the partly reduced acid, which was dissolved in caustic soda and the whole process repeated, so that in all 900 g. of amalgam were used. The oily acid was dried, dissolved in chloroform (3 vols.) in a freezing mixture, and a slight excess of 20% bromine in chloroform added. The 2 : 3-dibromo*cyclo*hexanecarboxylic acid (Aschan, *loc. cit.*) obtained by removal of the solvent had m. p. 167·5° after recrystallisation from benzene–petroleum (equiv. 285·6; calc., 286·0). Yield, 160 g. from 225 g. of benzoic acid (15 runs). 80 G. of this in 800 c.c. of absolute alcohol were treated under nitrogen with 30 g. (2 mols.) of zinc for 30 minutes at room temperature and 45 minutes on the steam-bath. The unsaturated acid was isolated in the usual manner; the atmosphere of nitrogen was maintained as far as possible to prevent oxidation to benzoic acid. Pure Δ^1-tetrahydrobenzoic acid (equiv. 126·2; calc., 126·1) was obtained in this way in 84% yield; the properties of two different preparations are given below :

Preparation.	B. p./mm.	M. p.	n.	d.	$[R_L]_D$ (Calc. 33·40).	B, %.
1	120°/10	7·0°	1·4814	1·0820	33·19	92·4
2	130/18	6·5	1·4813	1·0814	33·19	93·2

Aschan describes the acid as an oil, b. p. 234—235° (*loc. cit.*).

cis-1 : 3-cyclo*Hexanolide* (VII) *and* cis-3-*Hydroxy*cyclohexanecarboxylic *Acid.*—150 G. of *m*-hydroxybenzoic acid (Offermann, *Annalen*, 1894, **280**, 5) were reduced by sodium in boiling alcohol, following Perkin and Tattersall (*loc. cit.*), and gave 100 g. of mixed hydroxy*cyclo*hexanecarboxylic acids. The method of Balas and Sròl (*Coll. Czech. Chem. Comm.*, 1929, **1**, 658), which employs a platinum catalyst, was less satisfactory for large quantities. The mixed hydroxy-acids were heated at 170°/760 mm. for 30 minutes, and the product distilled. The lactone came over at 120—140°/20 mm., and a little *trans*-hydroxy-acid at 177—190°/20 mm. Redistillation of the low fraction gave the pure lactone, b. p. 120—123°/19 mm., forming rather sticky needles from petroleum (b. p. 60—80°), m. p. 119° (equiv., by back titration, 126·0; calc., 126·1). This was heated with a slight excess of caustic soda for 15 minutes, and the solution acidified and extracted with ether. The residue from the ether on recrystallisation from ethyl acetate gave pure *cis*-3-hydroxy*cyclo*hexanecarboxylic acid, m. p. 132° (Perkin and Tattersall give m. p. 130—132°).

Lactonisation of Δ^2-*Tetrahydrobenzoic Acid.*—Experiments with this acid and its isomeride were performed in an atmosphere of nitrogen. After treatment with boiling 50% sulphuric acid under Fittig's conditions (*Annalen*, 1894, **283**, 47), 73% of material was recovered which contained 63% of 1 : 3-*cyclo*hexanolide, identified by m. p. and mixed m. p. Longer treatment with boiling sulphuric acid resulted in gross decomposition. The acid passed into solution in 60% sulphuric acid (5 vols.) after 42 minutes at room temperature. A large amount of polymeric material was formed, but there was no charring.

			Composition of distillate.	
Time, hrs.	% Recovery (distillate).	B. p./mm.	% Acid.	% Lactone.
0·75	46	124—128°/15	89·5	10·0
2	33	122/15	73·5	26·0
4	25	125/12	11·0	88·5

After 4 hours the recovery was very poor but the product was almost pure lactone, which was identified by m. p., mixed m. p., and equivalent (126·2; calc., 126·1).

The Δ^2-acid was boiled alone under nitrogen for 1 hour. After distillation the product contained 99% of acid and 0·5% of lactone.

Attempted Lactonisation of Δ^1-*Tetrahydrobenzoic Acid.*—After 30 minutes' boiling with 50% sulphuric acid (5 vols.), 46% of distillate were recovered, b. p. 132—136°/13 mm., which contained 90% of acid, 8·5% of lactone. The acid was the pure Δ^1-isomeride (m. p. 37°), but insufficient lactone was isolated for identification. No lactone was formed when the Δ^1-acid was kept for 3 days at room temperature with 60% sulphuric acid, and the acid had not isomerised (m. p. 37—38°).

Reactions of 1 : 3-cyclo*Hexanolide.*—The lactone was completely destroyed by 30 minutes' boiling with 50% sulphuric acid. It was partly polymerised after 7 days' standing with 60% acid in the cold, but the monomeric material recovered (60%) was pure (m. p. 120°) and free from acid. The lactone was unchanged by 3 hours' boiling alone.

Hydrolysis and Formation of Hydroxy-acid.—The lactone was boiled with water under the

standard conditions (Boorman and Linstead, *loc. cit.*). Pure *cis*-3-hydroxy*cyclo*hexanecarboxylic acid was treated similarly.

Material.	Time, hrs.	% Acid.	% Lactone in product.
Lactone	24	74·7	25·5
,,	48	86·8	14·6
,,	96	90·1	12·6
,,	144	89·5	13·5
Hydroxy-acid	24	88·0	12·0
,,	72	87·3	14·2

Where the total of the values for acid and lactone exceeds 100%, it is probable that the direct titration figure (% acid) is more correct. A trace of ψ-acidic impurity appears to be formed in the longer experiments. The formation of lactone from hydroxy-acid under Hjelt's conditions was not measured owing to the very high proportion of hydroxy-acid at equilibrium.

Tautomeric Change between the Δ^1- *and the* Δ^2-*Acid in Alkali.*—This was followed under standard conditions (Linstead, J., 1927, 2579), but owing to the instability of the Δ^2-acid the boiling with alkali was carried out in sealed bulbs and the equilibrated acid was distilled in nitrogen. The composition of the mixture was determined by bromine addition, the following reference figures being used :

% Δ^2-acid	0·0	4·4	9·1	12·9	16·7
% Bromine added	1·7	6·5	10·8	14·0	18·2

The Δ^1-acid yielded 78% of a mixture of isomerides with equiv. 126·1 (calc., 126·1), B 5·9%, whence % Δ^2-acid = 4·1. The Δ^2-acid gave 74% of a mixture with equiv. 126·4, B 6·2%; % Δ^2-acid = 4·4. Both samples gave a considerable quantity of solid Δ^1-acid, m. p. 37°. The mobility was not determined.

trans-2-*Bromocyclo*hexanecarboxylic *Acid.*—Passage of dry hydrogen bromide into Δ^1-tetrahydrobenzoic acid in acetic acid yielded the 2-bromo-acid, which crystallised from petroleum in rosettes of flattened needles, m. p. 108° (equiv. 206·6; calc., 207·0). Aschan (*loc. cit.*) prepared this acid (m. p. 108—109°) by heating the same components in a sealed tube, which suggests that the acid has the *trans*-configuration. The acid was esterified by cold alcoholic sulphuric acid at room temperature (2 days) to the *ethyl* ester, which could not be distilled without decomposition (Found : Br, 33·9. $C_9H_{15}O_2Br$ requires Br, 34·0%).

cis-3-*Bromocyclo*hexanecarboxylic *Acid.*—The method of Perkin and Tattersall was improved as follows : A mixture of *cis*-1 : 3-*cyclo*hexanolide and water (1¼ vols.) was saturated with hydrogen bromide at 0°, kept in a closed vessel for 1 day, and again saturated at 0° and kept for a further 3 days. Water was added and the solid upper layer was crushed, collected, and dried on a tile over sulphuric acid in a vacuum desiccator. Yield, 85% of burr-like clusters of needles from light petroleum, m. p. 65° (lit. 62°) (equiv. 207·0; calc., 207·0). The *ethyl* ester, prepared in the same manner as the 2-bromo-isomeride in 96% yield, distilled without decomposition at 143°/25 mm. (Found : Br, 34·2%).

Addition of Hydrogen Bromide to Δ^2-*Tetrahydrobenzoic Acid.*—Analysis of the products was complicated by the possible formation of *cis*- and *trans*-bromo-acids, but a modification of the method previously used (Boorman, Linstead, and Rydon, *loc. cit.*) gave satisfactory results. A solution of the acid in alcohol (20 vols.) and water (40 vols.) was exactly neutralised with $N/10$-baryta, warmed on the steam-bath under reflux for 15 minutes, and again neutralised with baryta. The pure 2-bromo-acid gave figures corresponding to the formation of 77 ± 1% of hydroxy-acid, and a little pseudo-acid. *cyclo*Hexene was also formed. The *cis*-3-bromo-acid was converted quantitatively into lactone and the *trans*-isomeride was unaffected. A known excess of baryta was then added, and the mixture warmed on the steam-bath for 1 hour. This hydrolysed the γ-lactone and decomposed the salt of the *trans*-γ-bromo-acid. The excess of baryta was again titrated. This method was applied to the analysis of unknown mixtures in two ways; first directly, and secondly after the proportion of β-bromo-acid had been artificially increased by the addition of a known amount, about 25 or 30%. Typical results obtained by the two methods are tabulated below under the headings "Direct" and "Indirect."

The addition of hydrogen bromide was slow to dry Δ^2-tetrahydrobenzoic acid, but more rapid when ½% of water was present. The products were left in a vacuum until the weight was constant and then gave the following analytical figures :

			Bromo-acid in product.			
			Direct.		Indirect.	
No.	Condition of acid.	Equivalent (Calc., 207·0).	% 2-.	% 3-.	% 2-.	% 3-.
1	Dry	207·5	17·5	86·5 (?)	18·0	82·0
2	,,	205·4	13·0	81·0	19·0	81·0
3	Moist	210·0	16·5	82·0	18·5	82·0
4	,,	205·0	17·0	83·0	18·0	82·0

The product from experiment 1 contained 38·6% Br (calc. for $C_7H_{11}O_2Br$, 38·6%).

These results were confirmed as follows. The pure 2-bromo-ester was boiled with ethyl sodiomalonate in benzene for 24 hours; the product, b. p. 95°/15 mm., was identified as Δ^1-tetrahydrobenzoic ester by conversion into *trans*-hexahydrohomophthalic acid (m. p. and mixed m. p. 158°). The products of experiments (2) and (3) were esterified, and the mixed bromo-esters boiled with ethyl sodiomalonate in benzene for 24 hours. The unchanged 3-bromo-ester was isolated by distillation [Found : for a synthetic mixture containing 78% of *cis*-3-bromo-ester, 79% of 3-bromo-ester; for the ester from (2), 83·5% of 3-bromo-ester, for the ester from (3), 83·0% of 3-bromo-ester].

The hydrobromides after several weeks deposited first the impure *trans*-3-bromo-acid, m. p. 153—157° (compare Perkin and Tattersall, J., 1907, **91**, 495), and then the *cis*-3-bromo-acid, m. p. and mixed m. p. 65°.

2. 3-*Methyl*cyclohexenecarboxylic Acids.

Δ^1-*Acid* (IV*).—This was prepared from 3-methyl*cyclo*hexanone by the method used for Δ^1-tetrahydrobenzoic acid with the minor differences noted below. The ketone tended to yield high-boiling compounds in the presence of mineral acids and the cyanohydrin was therefore made as follows : The sodium bisulphite compound from 170 g. of ketone was treated with a solution of 104 g. (1 mol.) of potassium cyanide in 200 c.c. of water, together with 300 c.c. of ether, which removed a coating of cyanohydrin from the surface of the bisulphite compound. The mixture was shaken for 30 minutes in ice and then over-night mechanically. The cyanohydrin was isolated by means of ether and was not distilled in bulk, although it could be distilled in small quantities in the presence of a few drops of concentrated sulphuric acid at 133°/16 mm. The crude cyanohydrin was dehydrated by the method used by Ruzicka and Brügger (*loc. cit.*) for the lower homologue. 103 G. of unsaturated nitrile, presumably Δ^1- + Δ^6-, were obtained, b. p. 88—95°/17 mm. 50 Hours' boiling with 2 mols. of 10% aqueous caustic potash were required for its hydrolysis. The product was acidified in ice with hydrochloric acid *very cautiously* on account of the ease with which the Δ^2-acid lactonises. A 77% yield of crude acid, b. p. 126—128°/7 mm. or 145—146°/15 mm., was obtained (equiv., 141·0; calc., 140·1). Bromine titration indicated that this contained about 22% of Δ^β-acid. The acid was partly esterified in the cold for 20 hours by the method described for the lower homologue; the ester (A) was retained and the unesterified acids (Δ^1- and Δ^6-) were separated through the calcium salts by the method of Perkin and Tattersall (*loc. cit.*). The less soluble calcium salt after crystallisation yielded 50 g. of 3-methyl-Δ^1-*cyclo*hexenecarboxylic acid, b. p. 130°/7 mm., which solidified in ice and melted at 26°. Perkin and Tattersall state that they were unable to obtain a completely solid acid by the calcium salt separation, and in view of this a small amount of the acid was converted into 1 : 2-*dibromo-3-methyl*cyclohexanecarboxylic acid, which formed small white plates from formic acid, m. p. 119° (Found : Br, 53·2; equiv., 300·0. $C_8H_{12}O_2Br_2$ requires Br, 53·3%; equiv., 300·0). On reduction with zinc and alcohol this regenerated an unsaturated acid identical in properties with the initial material. Hence, purification by partial esterification and through the calcium salt suffices to yield the homogeneous Δ^1-acid, which has m. p. 26—27°, n 1·4917, d 1·0501, $[R_L]_D$ 38·62 (calc., 38·02), B 2·0%.

Δ^2-*Acid* (II).—This was obtained by Perkin and Tattersall (*loc. cit.*) in an impure form from the corresponding 3-bromo-acid. The crude ester (A) obtained during the purification of the hydrolysis product of the unsaturated nitrile described above (24 g.) was hydrolysed in the manner described for *iso*hexenoic acid (J., 1932, 125). The acid had b. p. 123°/7 mm. (equiv., 140·9; calc., 140·1). As the low bromine addition (79·4%) suggested that some Δ^α-acid was still present, the acid was separated by partial esterification for 4 hours into an ester (B) and an acid (C).

* Perkin and Tattersall call this the Δ^6-acid, the acid (V) being the Δ^1-; but this is inconvenient for the present purpose.

The acid (C) was in turn esterified for 6 hours to give an ester (D). Both (B) and (D) gave on hydrolysis the almost pure Δ^2-acid with bromine additions of 96·1 and 95·1%. Total yield, 11·2 g. A solid dibromide was not obtained, but the acid readily yielded a *p*-toluidide, tufted needles from light petroleum, m. p. 108—109°.

1-*Methyl*-1 : 3-cyclo*hexanolide* (VIII).—This was prepared from *cis*-3-hydroxy*cyclo*hexane-carboxylic acid following Perkin and Tattersall. The 3-hydroxy-3-methyl*cyclo*hexanecarboxylic acid from this was distilled slowly in a vacuum, 4·6 g. of a fraction, b. p. 128°/22 mm., being obtained (Perkin and Tattersall give b. p. 145°/20 mm.). This was dissolved in ether, washed with sodium bicarbonate solution, and left in contact with potassium carbonate in a vacuum. Distillation then yielded pure *cis*-1-methyl-1 : 3-*cyclo*hexanolide, b. p. 120—121°/20 mm., which solidified to a mass of overlapping plates, m. p. 45° (Found : C, 68·3; H, 8·5. Calc. : C, 68·4; H, 8·6%). Another preparation of the same solid lactone is described below.

No lactonisation of the Δ^1-acid was effected by the action of sulphuric acid either at the boiling point for 15 minutes or in the cold for 7 days under the usual conditions.

Lactonisation of the Δ^2-Acid.—(i) The acid was charred by hot dilute sulphuric acid. It rapidly dissolved in 5 vols. of 60% sulphuric acid at 20°, with a rise in temperature of 5°. The following samples were analysed :

Time, mins.	% Recovery (distillate).	B. p./mm.	Composition of distillate.	
			% Acid.	% Lactone.
5	89	118/18	15·5	86·0
15	86	,,	12·5	88·5
60	83	,,	8·5	92·5

The products were combined and separated into acid and lactone. The small amount of acid had the bromine addition of the unchanged Δ^2-acid (96%). The lactone had m. p. 44°, alone or mixed with 1-methyl-1 : 3-*cyclo*hexanolide (equiv., 139·8; calc., 140·1). This showed that the Δ^2-acid was substantially free from the Δ^6-isomeride.

The easy preparation of lactone by this process suggested that it might also be obtainable from the mixture of methyl*cyclo*hexenecarboxylic acids obtained from 3-methyl*cyclo*hexanone through the cyanohydrin, which was known to contain about 22% of Δ^β-acid (p. 264). 55 G. of this mixture were shaken vigorously for 15 minutes with 60% sulphuric acid (5 vols.). The lactone, isolated and freed from acid as usual, boiled at 100°/8 mm. (7·5 g.), and had m. p. 44° and mixed m. p. 45°. The fact that the lactone was the pure 1 : 3-isomeride shows that there was no tendency for any other isomeric acid to lactonise under these conditions. Moreover the amount of lactone isolated (corrected for experimental losses obtained when lactonising the pure Δ^2-acid under the same conditions) corresponded to a content of 19% of Δ^2-acid in the original mixture, *i.e.*, nearly as much as that indicated for the *total* Δ^β-acid by bromine titration Hence the amount of Δ^6-acid present in the mixture must be very small.

(ii) The acid was boiled gently in an all-glass apparatus in an inert atmosphere with the following results :

Time, mins.	30	90	120 *	300
Product { % acid	74	68	72	65
% lactone	26	31·5	32	30·5

* This product was distilled before analysis. The lactone, separated in the usual manner, had m. p. and mixed m. p. 44°.

Reactions of 1-Methyl-1 : 3-cyclohexanolide.—(i) The lactone was boiled under the same conditions as the Δ^2-acid and the products were analysed without distillation.

Time, mins.	75	255	375
Product { % acid	42·5	61·5	57·5
% lactone	58	36·5	36·5

A sample of lactone was boiled for 300 minutes and the acid that had been produced was separated in 63% yield. It had a bromine addition of 94%. This was converted into the *p*-toluidide, which crystallised from light petroleum as a mixture, m. p. about 100°. Owing to lack of material the nature of the isomeric acid could not be determined more precisely.

(ii) The lactone was charred by the action of hot dilute sulphuric acid, but not so readily as the isomeric Δ^2-acid. It was unaffected by cold 60% sulphuric acid.

(iii) When boiled with water, it yielded the corresponding hydroxy-acid as follows :

Time, hrs.	42	48	72
Product { % hydroxy-acid	21·6 (?)	27·1	28·7
{ % lactone	74·0	75·2	69·3

The formation of the lactone from the hydroxy-acid at 100° was followed by the usual method (J., 1932, 128), with these results :

Time, mins.	20	65	185	365	545
% Lactone formed	5·2	15·2	35·1	47·7	54·1

The time of half-change to the equilibrium is 198 minutes.

Tautomeric Change of the Δ^1- into the Δ^2-Acid in Alkali.—The mobility was remarkably low. Pure Δ^1-acid was boiled for 16 hours (copper flask) with 2 mols. of 25% caustic potash solution. The acid was isolated as usual : 90%, equiv., 140·4 (calc., 140·1), B 6·2%. After further treatment with 2 mols. of 40% caustic potash solution for 64 hours, 84% was recovered with equiv. 141·0, B 13·0%. This was finally boiled for 90 hours with 3 mols. of 33% caustic potash solution and then had equiv. 141·1, B 27·0% ; 84% recovery. A second sample was boiled successively with caustic potash as follows : (i) 9 hours with 10 mols. of 25% ; 63 hours with 2 mols. of 40% ; 114 hours with 3 mols of 33%. An overall yield of 55% was obtained with equiv. 140·4, B 26·0%. The second treatment was much more drastic, but the final products had very similar bromine additions and were therefore presumed to have reached the equilibrium at a value of 74·8% of Δ^1-acid. The Δ^2-acid was isolated from the equilibrium mixture in the manner described under its preparation and gave the same *p*-toluidide, m. p. and mixed m. p. 109°.

2-Bromo-3-methylcyclohexanecarboxylic acid (probably *trans*-) was prepared by saturating a mixture of 3-methyl-Δ^1-*cyclo*hexenecarboxylic acid and an equal part of glacial acetic acid at 0° with hydrogen bromide and keeping the solution for a few days. The solvent was removed, and the resulting solid pressed on a porous tile and crystallised from light petroleum. The bulk of the product formed needles, but small amounts of a second form crystallising in long prisms were obtained (? the *cis*-acid). The needles melted at 144·5° (Found : Br, 36·2; equiv., 221·3. $C_8H_{13}O_2Br$ requires Br, 36·2% ; equiv., 221·0).

cis-*3-Bromo-3-methylcyclohexanecarboxylic acid* was made by treating 3-methyl-1 : 3-*cyclo*hexanolide with 2 vols. of aqueous hydrogen bromide, saturated at 0°, for 48 hours. The bromo-acid, isolated by means of ether, soon solidified to a mass of needles, m. p. 45° after being drained on a tile (Found : Br, 35·8. $C_8H_{13}O_2Br$ requires Br, 36·2%). The substance very readily re-formed the lactone with loss of hydrogen bromide. It was soluble with immediate decomposition in water (like γ-bromo*iso*hexoic acid) and the equivalent could not be determined.

Addition of Hydrogen Bromide to 3-*Methyl-*Δ^2-*cyclohexenecarboxylic Acid.*—Mixtures of the 2- and the 3-bromo-acid were analysed by the following process. A weighed amount of the bromo-acid was dissolved in alcohol and water and neutralised with $N/10$-baryta. The solution was boiled under reflux for 30 minutes and again titrated with baryta. The pure 2-bromo-acid yielded 97·5% of hydroxy-acid, no ψ-acid, and a trace of unsaturated hydrocarbon. The 3-bromo-acid yielded no acidic material, the barium salt being stable. For an artificial mixture containing 90·5% of the 3-bromo-acid, the percentage found was 90·4.

The addition of hydrogen bromide to dry Δ^2-acid and to acid containing $\frac{1}{2}$% of water was carried out in the usual manner, and the product analysed by the above method [Found : (dry addition) 99·1, 99·1% of 3-bromo-acid; (moist addition) 99·0% of 3-bromo-acid]. The combined products were boiled with caustic soda for 10 minutes, acidified, and extracted with ether. The product was distilled, freed from traces of acid with sodium bicarbonate, and redistilled. 1-Methyl-1 : 3-*cyclo*hexanolide was obtained, m. p. and mixed m. p. 45°, which showed that a considerable quantity of the 3-bromo-acid had the *cis*-configuration.

3. α-*Methylpentenoic Acids.*

Preparations (Goldberg and Linstead, *loc. cit.*).—190 C.c. of propaldehyde yielded 34 g. of Δ^α-acid. This was not appreciably purified by partial esterification. It had m. p. 101°/9 mm., m. p. 21°, *n* 1·4583, *d* 0·9829, $[R_L]_D$ 31·71 (calc., 30·98), *J* 0·6%, equiv. 113·9 (calc., 114·1). Reduction of ethyl α-methyl-β-acetosuccinate yielded 57% of αγ-dimethylparaconic acid, which was pyrolysed to crude α-methyl-Δ^β-pentenoic acid. This was partly esterified for 5 hours, and the ethyl ester hydrolysed to the pure acid (25% yield from the paraconic acid), b. p.

90°/10 mm., *n* 1·4360, *d* 0·9619, [*R*_L]_D 31·02, *J* * 75·0%, equiv. 113·9, which failed to solidify after 24 hours at − 80°.

Lactonisations.—(1) Δ^α-*Acid.* There was no gross decomposition with boiling 50% sulphuric acid and the formation of lactone proceeded as follows :

Time, mins.	% Recovery (distillate).	B. p./mm.	Composition of distillate.	
			% Acid.	% Lactone.
15*	90	98—102°/7	96·0	5·5
90	89	85—108/11	44·5	55·5
360	84	85/11	2·5	97·0

* Fittig's conditions (*loc. cit.*).

The products were combined and separated into acid and lactone. The acid had b. p. 103°/10 mm., *n* 1·4579, *d* 0·9826, *J* 0·6%, equiv. 114·1. It melted at 20° alone or mixed with the Δ^α-acid. The lactone had b. p. 81°/10 mm., *n* 1·4289, *d* 1·0036, whence [*R*_L]_D 29·29 (calc., 29·37), equiv. 114·2 (calc., 114·1). It solidified in solid carbon dioxide–ether to a crystalline mass, m. p. − 36°. The identity with the α-methyl-γ-valerolactone of Blaise and Luttringer (*loc. cit.*) was confirmed by preparation of the hydrazide, m. p. 118°, from ethyl acetate (lit., 115°). Cold dilute sulphuric acid had no action on the acid.

(2) Δ^β-*Acid.* After treatment under Fittig's condition the acid yielded 89% of distillate, b. p. 84°/10 mm., containing 2% of acid and 98·5% of lactone. After purification the lactone was proved to be identical with α-methyl-γ-valerolactone by m. p. and mixed m. p. (− 37°) and other physical constants, which were almost the same as those given above. Treatment with cold 60% sulphuric acid gave the following results : there was no rise in temperature and the two acids mixed only slowly.

Time, hrs.	% Recovery (distillate).	B. p./mm.	Composition of distillate.	
			% Acid.	% Lactone.
2	75	84—90°/10	55·5	45·5
5	81	82/9	26·5	74·5
24	83	87/9	3·5	98·5

The unlactonised acid was identified as the Δ^β-isomeride by its physical properties and iodine addition. The lactone was identical with that already described (m. p. and mixed m. p. − 36°).

The Δ^β-acid was boiled for 3 hours under atmospheric pressure and then distilled at 92°/11 mm. There was hardly any lactonisation (acid, 98·2%; lactone, 2·5%).

Reactions of α-Methyl-γ-valerolactone.—The lactone was unchanged after treatment for a week at room temperature with 60% sulphuric acid or for 90 minutes at the b. p. with 50% acid. The hydrolysis of the lactone by boiling water (*a*) and the velocity of its formation from the hydroxy-acid (*b*) were determined by the standard methods :

(*a*) Time, hrs.			24			48		
% Acid......................			2·0			2·0		
% Lactone			—			96·0		
(*b*) Time, mins.	5	10	15	30	45	60	120	240
% Lactone formed	18·4	34·5	43·3	61·8	71·4	78·2	87·0	93·0

Preliminary experiments on the addition of hydrogen bromide to α-methyl-Δ^β-pentenoic acid indicated that about 90% of the γ-bromo-acid was formed. The product was converted in good yield into α-methyl-γ-valerolactone, identified by m. p. and mixed m. p.

* This iodine addition is considerably higher than that observed by Goldberg and Linstead and partial esterification has obviously eliminated some Δ^α-isomeride. In view of the fact that unsaturated acids are isomerised at high temperatures (Linstead, J., 1930, 1603; Linstead and Noble, *loc. cit.*), it is not surprising that some Δ^β-acid should have changed into the stable Δ^α-form at the temperature of pyrolysis (290°). On the basis of the new value for the iodine addition of the Δ^β-acid the position of the three-carbon equilibrium has to be corrected from 81% αβ- to 89% αβ-. If this is compared with the figure for the *n*-pentenoic acids (68% αβ-; Linstead and Noble, *loc. cit.*), it will be seen that the effect of the α-methyl group in stabilising the αβ-position of the double bond is even greater than at first thought.

The Process of Coagulation in Smokes.

THE FIFTH LIVERSIDGE LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY ON FEBRUARY 14TH, 1935.

By PROFESSOR R. WHYTLAW-GRAY, O.B.E., F.R.S.

OF the various classes of disperse system known to colloid chemistry, that in which the medium is a gas has until recently attracted little attention. This is the more remarkable because aerial types are of such common occurrence and they should be relatively simpler than hydrosols and easier to interpret. Systems of this type, though presenting certain analogies with true colloids, differ from them sharply and definitely by one outstanding characteristic, *viz.*, their instability.

The ultramicroscopic particles in gold sols, for instance, remain in suspension for indefinite periods, and it is only by experiments at strictly controlled temperatures that it is possible to detect a separation by sedimentation of the two phases. Further, the particles in such a sol, though in active Brownian movement, never approach close enough to collide but are held apart by ionic forces. It is only when, by the addition of electrolytes, the isoelectric point is approached, that coagulation takes place and the sol precipitates.

Aerial disperse systems behave in a totally different manner : not only do the particles sediment more rapidly, but collisions under Brownian movement cause them to cohere so that the system rapidly becomes coarser and finally flocculates out.

No instance has been discovered of an aerial or gaseous disperse system which is not undergoing spontaneous coagulation. This difference is fundamental, and sharply differentiates the two types. It is clearly due to the difference between the media, water and air. Not only do these differ widely in density and viscosity, but even in the purest water the concentration of the ions is very much greater than in air. In consequence, the Brownian motion and rate of sedimentation in gaseous media are very much more rapid than in liquids, and no counterpart of the ionic micelle with its electric double layer has been detected. Indeed, in smokes and many aerosols, oppositely charged as well as unelectrified particles can exist for long periods in the same system and in many cases the electrification has little influence on the rate of coagulation. The particles in smokes are on the average about ten times larger than in colloids and, in general, have radii between 5×10^{-6} and 5×10^{-5} cm. $(0.05—0.5\mu)$.

The one property, then, which determines to a large extent the behaviour of all aerial or gaseous systems such as smoke, fume, dust, or fog is this property of continual coagulation, and a study of the process is important because all the properties dependent on particle size are determined by it.

The first clear indication that smokes coagulate was obtained by Tolman and his coworkers in 1919 (*J. Amer. Chem. Soc.*, **41**, 297, 575, 587) by the measurement of the variation with time of the intensity of the Tyndall beam. Various smokes were dispersed thermally in a large metal chamber, and it was found that for any one smoke the tyndallmeter readings decreased with time more rapidly than the weight of smoke material in suspension. Now, by independent experiment, it was found possible to correlate the tyndallmeter readings with (*a*) mass concentration, and (*b*) average size of particle, and it was evident that the decrease noted could only be explained by coagulation.

These experiments, however, gave no information about the number of particles present or their actual size, and afforded no means of comparing different smokes. The first attempt to apply Zsigmondy's slit ultramicroscope to the counting of smoke particles was made in 1923 (Whytlaw-Gray, Speakman, and Campbell, *Proc. Roy. Soc., A*, **102**, 600), and it was soon found that dense smokes similar to those used by Tolman, of a mass concentration of the order of 1 g. per cubic metre, were unsuitable because the particles were too large and too heterogeneous. A suitable mass concentration proved to be about 20 mg. per cubic metre. This weight was dispersed quickly inside a cubic-metre glass chamber by volatilisation either from an electrically heated boat, in the case of substances like ammonium chloride, resin, paraffin, etc., or from an arc, when oxide or metal smokes

were used. During dispersal, the smoke was mixed rapidly with air by means of an electric fan in the chamber.

In the first experiments of this kind, when organic substances of high boiling point were used to produce the smoke, it was found that the number of particles, initially about 1—2 million per c.c., diminished very rapidly for the first hour and thereafter at a slowly decreasing rate, but after 7 hours the air of the chamber still contained many thousands per c.c., and even after 24 hours the presence of particulate matter was usually clearly visible in the Tyndall beam. In normal light these smokes were quite transparent and no haze was noticeable.

In order to determine what fraction of the material originally dispersed remained in suspension at different periods during the life of the smoke, one litre was filtered off from time to time through small asbestos filters which were weighed on a microbalance (Whytlaw-Gray and Speakman, *ibid.*, p. 615). It was then found that the change in mass was small during the early period when the decrease in number was very rapid. This observation proved clearly that, unless the particles were disappearing by evaporation, coagulation was taking place. An examination of a series of oxide smokes set these doubts at rest : there could be no possibility of the evaporation of smoke particles of the oxides of magnesium, copper, or zinc. From these data, too, the average weight of the particle could be calculated and an estimate made of its size.

Knowledge of the form and degree of complexity of the aggregates was obtained (Whytlaw-Gray, Speakman, and Campbell, *ibid.*, p. 613) by exposing glass slides to the smoke and examining the deposits with the microscope under dark-ground illumination. In fine smokes, only minute diffraction discs were visible at first, but later, the discs became brighter and increased in size just as did the suspended particles seen in the slit ultramicroscope. When, however, much denser smokes were used, the increase in complexity of the aggregates with time was clearly marked, and these in many oxide smokes exhibited a remarkable chain-like structure; this was particularly noticeable with the oxides of zinc, cadmium, magnesium, aluminium, and antimony. At high concentration these oxides aggregate finally to loose and flock-like complexes composed of a vast number of irregular strings and chains. As Kohlschütter and Tüscher (*Z. Elektrochem.*, 1921, **27**, 1) have shown, these, when collected in bulk by electrical precipitation, have a remarkably low density, much smaller than that of the oxides prepared in the usual way; further, when treated with water or dilute alkalis, the complexes often disintegrate and form colloidal solutions or fine suspensions. This is especially marked with smokes composed of the oxides of tin, iron, antimony, and silicon.

In an electric field, the particles which are highly charged in the arc smokes build up on the electrodes long strings or chains which often take the shape of tree-like growths. In a gentle stream of air some of the branches can be made to rotate continuously, the trunk and other branches remaining stationary. This behaviour, and also the peptisation in dilute alkalis, was regarded as lending support to the view that the single particles composing the chains are separated from each other by films of adsorbed air. By using a more elaborate technique, it has been found possible to examine the particles in dilute clouds at high magnification by transmitted light : those in arc smokes consist largely of small chains, sometimes with invisible material between the links.
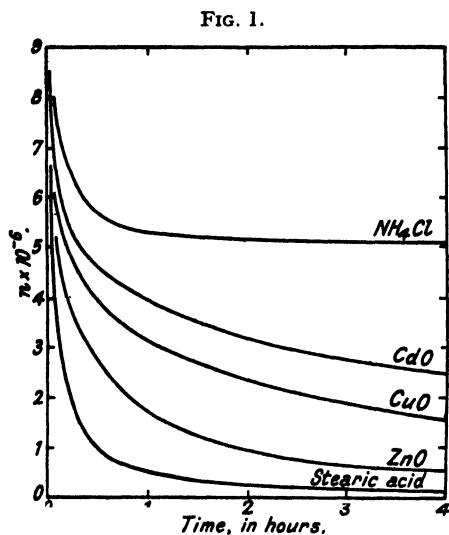
Much more compact aggregates, roughly spherical, are formed by substances which volatilise at a lower temperature, such as arsenic trioxide, mercuric chloride, resin, stearic acid, and many organic dyestuffs. The density and radii of the complex smoke particles can be determined by an inversion of Millikan's method for finding the charge on the electron (Patterson and Whytlaw-Gray, *Proc. Roy. Soc.*, 1926, *A*, **118**, 302). The particle carrying a known number of electrons is balanced against gravity in an electric field of known strength, and then its velocity under gravity alone is measured. The electronic charge being assumed, the density and radius can be calculated. It was found that, whilst minute droplets of paraffin oil gave a normal value for the density, yet the particles in arc clouds were on the average about one-tenth of the normal, though occasionally, even in these smokes, particles approaching a normal density were found, especially among the very small ones.

Of the easily volatilised substances only mercuric chloride was examined in this way. Its mean density was found to be about one-quarter of its bulk density, an observation in close accord with its compact structure under the microscope.

It might be thought that the high charges carried by these particles determine to some extent the structures we have described. This, however, is certainly not the case for zinc oxide, for unelectrified clouds of this substance, prepared by the interaction of the vapour of diethylzinc with air, give complexes and chains of exactly the same character and appearance under the microscope as those just described. It seems probable that the particles in the chains and strings are minute crystals too small to be resolved by the microscope, which are held together by polar forces acting along crystal axes or even by amicroscopic threads of crystalline material. The crystalline nature of many smoke films has been proved by Finch (*Proc. Physical Soc.*, 1934, **46**, 148) by means of an electron-diffraction method, and he has established the structure of films of zinc oxide. Walmsley, too, has studied cadmium oxide complexes by an X-ray method and has determined the probable orientation of the crystals in the chains (*ibid.*, 1928, **40**, 7).

FIG. 1.

Slit ultramicroscope curves compared with standard curve for stearic acid.

Returning now to coagulation, it is of importance to determine the true course of this process, to find out if it varies with the size and nature of the particles, and if it is analogous to the corresponding process in colloids. Before this can be done it is essential to be able to determine the true variation with time of the number of particles, *i.e.*, the form of the coagulation curve.

With the object of improving the ultramicroscopic method, the original instrument was replaced by one of improved design provided with a lens system of higher optical aperture and illuminated by an automatic arc instead of a pointolite lamp. A number of dilute smokes were then examined and counted, and the number–time or " particulate number " curves plotted (Fig. 1). These showed the same features as the earlier graphs, but indicated that the course of coagulation varies from smoke to smoke, especially in the later stages. At the time it was believed that these graphs were at least approximately correct, but subsequent experience has proved that they present a totally erroneous picture of the coagulation process.

In order to check the accuracy of these counts, a sedimentation method was developed, in which a small sample of smoke could be enclosed between two glass plates without causing disturbance. This was done by sliding the plates along the upper and lower surfaces of a horizontally placed rectangular sheet of brass 2 mm. thick, which was pierced by a hole of about 1 cm. in diameter. When the glass plates were pushed over the hole a small cylindrical segment of smoke was enclosed, and on standing, the particles settled out on the under plate in the form of an even deposit; usually a few particles were caught on the upper surface by diffusion. The particles in the deposit could be easily counted with the microscope when illuminated suitably.

A series of these " collector slides," as we have called them, were constructed and placed inside the smoke chamber, and the plates drawn at any suitable time. The method gave numbers in close agreement with the counts obtained with the first ultramicroscope, but very much smaller than those with the improved instrument.

It was thought that small particles might become invisible on settling on a glass surface. A direct experiment in which the particles could be observed as they settled showed that they vanished from sight only if they were liquid—solid particles remained clearly visible

down to very small dimensions. Thus, many of the particles in tobacco smoke disappear as they settle, others diminish in brightness, but cadmium oxide particles even in fine smokes are easily seen after settling, provided the glass surface is clean and free from dots and striæ. One of the great difficulties of the method is to obtain glass surfaces so perfectly polished that even in intense illumination they show no imperfections simulating particles.

For the detection of the finest particles, we have found that the most effective dark-ground illumination is furnished by a convergent beam of light from an arc directed on to the deposit at an angle of 30°. Through the kindness of Sir Herbert Jackson, we were finally able to procure nearly perfect glass surfaces. A comparison of the two methods again indicated a similar divergence, as shown in the following table.

Comparison of counts on the same smoke made by collector slide and slit ultramicroscope methods.

Time, minutes	4	10	20	40	60
Number per { Slit ultramicroscope...	2·75	2·15	1·63	1·15	0·9
c.c. × 10⁻⁶ { Collector slide	2·15	1·47	0·78	0·45	0·32

In the meantime the possibility of particles being counted outside the illuminated ribbon of light in the slit ultramicroscope was investigated. With intense illumination, an error of this kind may arise from stray light reflected from the walls of the cell itself or from smoke particles outside the field of vision, especially in the later stages when the complexes are bright. Any extraneous light would extend the visibility outside the measured zone and give rise to counts which are too high. Westgren (*Arkiv Matem. Astron. Fys.*, 1918, **11**, No. 8), in counting gold sols, drew attention to this error, and more recently Tuorila (*Kolloid-Z.*, 1926, **38**, 16), who checked the readings of the slit instrument against a cardiod ultramicroscope, found a constant difference between the two, the former giving counts four times as great as the latter. In smokes, with their much larger particles, this error appears to be of greater significance than in sols.

Fig. 2.

Our experiments cast grave doubts on the reliability of the counts made in smokes with the slit ultramicroscope, and led us (Nonhebel, Colvin, Patterson, and Whytlaw-Gray, *Proc. Roy. Soc.*, 1927, *A*, **116**, 542) to design a cell in which the depth was strictly defined, as in the cardiod, by the distance between the cell walls instead of by the optical boundaries of the image of the slit.

The essential features of the cell will be clear from the accompanying diagram (Fig. 2). The count is made when the smoke is between the parallel portions of the two glass surfaces, the distance between which can be as small as 0·1 mm. A current of smoke is passed through the cell and stopped intermittently by means of a slowly rotating tap so that the small element of smoke to be counted only remains in the narrow part for a small fraction of a second. The proportion of particles diffusing to the walls in the narrow space before the count is made is inconsiderable. Full details of the method have been described elsewhere.

After gaining experience with the new cell by counting a number of smokes and improving the experimental technique, we were in a position to compare the data it furnished with those given by the collector-slide method. When a fine cadmium oxide smoke was used for a series of clouds, a good agreement was obtained, which was quite satisfactory in view of the fact that the experimental errors in the two methods differ widely. Below are given the data obtained from a single experiment:

Cadmium oxide smoke.

Time, minutes	8	24	43	62	84
Number per { New cell..................	0·88	0·51	0·34	0·26	0·20
c.c. × 10⁻⁶ { Collector slides	0·92	0·47	0·33	0·24	0·21
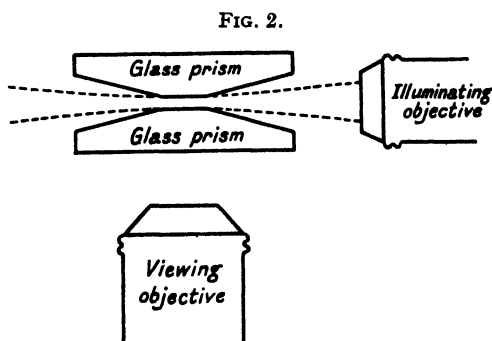
A further confirmation of the reliability of the data obtained with the new cell is afforded by the results of an extremely elegant method of counting smoke particles, devised independently by Green (*Phil. Mag.*, 1927, **4**, 1046), in which a modified Wilson expansion apparatus is used. A cell similar to that employed in the slit ultramicroscope is arranged so as to form the upper part of the cylinder of a small expansion apparatus, and on expansion the smoke particles are instantaneously loaded with moisture and grow to a comparatively large size, whereupon they can be easily photographed. Since the droplets are large and bright, a narrow beam of light of low intensity can be used; moreover, it is easy to exclude particles outside the depth of focus of the microscope, and the error inherent in counting diffraction images with the slit ultramicroscope does not arise. The method, too, has the advantage of being able to detect and enumerate amicroscopic particles, and also small ultramicroscopic ones which, on account of their vivid Brownian motion and low visibility, are very difficult to perceive when using the direct ultramicroscopic method.

Green's method was found to agree satisfactorily with the two methods just described. Hence, there are now three independent ways of counting the particles in smoke clouds, and they all yield substantially the same result, account being taken of the comparatively large errors inherent in work of this character.

The agreement between these different ways of counting smoke particles has been emphasised because the form of the particulate-number curve is of importance for the correct interpretation of the process of coagulation. For instance, if the graphs in Fig. 1 were assumed to be accurate, it would be concluded that coagulation ceased or became very slow when the complexes reached a certain size depending on the nature of the smoke substance; *e.g.*, the ammonium chloride smoke apparently becomes stable after an hour, when the number of particles is about 5×10^6 per c.c., whilst cadmium oxide seems to stabilise at a much lower figure. If, however, the curves obtained by counting with the new cell are compared, we find that they are all closely similar to each other and show no sign of stabilisation. The type of curve is at once evident if, instead of the number of particles per c.c., its reciprocal is plotted against time, whereby in nearly all cases a straight line is obtained.

FIG. 3.

Particulate-volume graphs for various smokes.

If n is the number of particles per c.c. at any time t, and n_0 the number present immediately the smoke is formed, then

$$1/n - 1/n_0 = Kt, \text{ or, if } 1/n = \sigma \text{ and } 1/n_0 = \sigma_0, \sigma - \sigma_0 = Kt,$$

where σ has a definite physical meaning and represents the volume on the average inhabited by a particle in the smoke. It is conveniently termed the "particulate volume," and as coagulation proceeds it increases linearly with time. For ordinary smokes of a mass concentration of the order we have used, the lines are straight or almost so within the limits of accuracy of the experimental points. Their slopes provide a means of classifying or comparing different smokes. The equation is of the same form as that established by Rutherford in 1897 for the rate of combination of small ions, and was later shown by Kennedy to be valid for the combination of large atmospheric ions, and also by Nolan for the rate of disappearance of nuclei, but naturally, on account of the smaller mobilities, the constant K is smaller for smokes than for ions.

It is remarkable that the coagulation constants for different smokes all lie fairly close to each other. In the table below are collected the constants for a variety of smokes

which we have determined. The weight concentrations (mg./cu.m.) are given in parentheses.

Coagulation constants for various smokes (in cm.³/sec. × 10⁹).

	K.		K.
Magnesium oxide	0·8	*Stearic acid (15 mg.), blown	0·51
Cadmium oxide (50 mg.)	0·8	*Oleic acid (15 mg.), blown	0·51
*Ferric oxide (16 mg.)	0·66	Paraffin oil (15 mg.), blown.........	0·50
Ammonium chloride (15 mg.)	0·60	*p*-Xyleneazo-β-naphthol (15 mg.)	0·63
*Resin (15 mg.), blown	0·49	Antipyrine (40 mg.)	0·57

Some of these numbers are only approximately correct. The well-established ones are marked with an asterisk.

The rate of coagulation depends on the method used for dispersal : some methods give smokes which initially may consist of even-sized particles; others tend to yield dispersions which are widely heterogeneous. Again, the rate of coagulation depends considerably on the average size of the particle. It is possible, however, to a large extent, to determine experimentally the influence of these factors. Thus, with ammonium chloride dispersed under strictly controlled conditions of temperature and rate of admixture with air, the initial number of particles does not vary much when the mass of the material volatilised is changed considerably. It is, hence, possible to determine the influence of size on the rate of coagulation.

Numerous careful experiments have been made with this object. Thus with ammonium chloride (Patterson, Whytlaw-Gray, and Cawood, *Proc. Roy. Soc.*, 1929, *A*, **124**, 504), a series of six different concentrations was investigated, *viz.*, 60, 30, 15, 7·5, 3, and 1 mg. per cubic metre, and a number of clouds at each concentration counted. Equality of numbers at the start being assumed, the average radii are roughly in the proportion of 4 : 3 : 2·5 : 2 : 1·4 : 1. The actual mean radii when the smokes contained 1 million particles per c.c. range from 21×10^{-6} cm. for the 60 mg. concentration to $5·4 \times 10^{-6}$ cm. for the 1 mg. smoke.

These sizes are calculated on the assumption that the density of the particle is normal, which for this substance in the early stages of coagulation is not far from the truth. A series of six particulate-volume graphs was obtained of gradually increasing slope as the concentration diminished; the lines for the two lowest concentrations were distinctly curved towards the time axis. The K values, which in the case of the two lowest concentrations were computed from the earlier points, were 0·55, 0·61, 0·70, 0·87, 1·30, and $1·70 \times 10^{-9}$. Although no accuracy is claimed for these figures, and probably the last two are much too great, they do show clearly that the coagulation rate increases rapidly as the average particle size falls. These smokes were heterogeneous and the values for K were abnormal. Considerable difficulty was experienced at first in counting the very fine particles in the 1 mg. cloud, for although they could be seen, it was not easy to enumerate them. It was found possible to transform them into minute droplets before they entered the counting cell by lining the entrance tube with damp filter-paper; the particles then grew to a size which was easily visible.

A confirmation of the greater coagulation rate of small particles can be deduced from the work of Flower (*Phil. Mag.*, 1928, **5**, 1084) on the fine particles given off by a heated platinum wire. These were just on the limit of visibility in the ultramicroscope, and at first only the larger were visible, the numbers increasing as coagulation proceeded. Finally, they were counted by Green's method. The graph of the particulate volumes against time was a straight line, the constant of which was $1·5 \times 10^{-9}$ cm.³/sec.

In some of our experiments we found that a very fine smoke was obtained when a stream of carefully filtered air was passed through an electrically heated metal tube. No matter what precautions were taken to clean the tube or to purify the air, Green's apparatus showed the presence of a large number of particles ("X smoke") which, however, were quite invisible in the ultramicroscope. A strong Tyndall beam did, however, indicate faintly the presence in the chamber of particulate matter. The cloud coagulated very rapidly, and the graph showed a slight curvature. The constant was found to be $3·2 \times 10^{-9}$ cm.³/sec. Collecting together the results for these very small particles, we have :

Coagulation rates for very small particles (K × 10⁹, cm.³/sec.).

Particulate system.	Size, cm. × 10⁻⁶.	K × 10⁹.	Particulate system.	K × 10⁹.
NH₄Cl (1 mg. per cu. m.)	5	1·7	Atmospheric nuclei (Kennedy)	1·3
Platinum	2·2	1·5	Small ions	1600
X Smoke	—	3·2	Small ions and nuclei (Nolan)	5000

It is of interest to compare these values with those of Kennedy (*Proc. Roy. Irish Acad.*, 1916, *A*, **33**, 66) for large ions and of Nolan for the rate of combination of small ions and nuclei.

In interpreting these figures, it must be borne in mind that the value of K depends on the rate at which the particles disappear, and the disappearance may be the result of evaporation as well as of coagulation. Small particles of substances of vapour pressure as low as 1×10^{-5} mm. of mercury evaporate at a noticeable rate when suspended in air. Evaporation can be followed conveniently by determining on the same particle the change with time of the rate of fall, and finding the radius by the Stokes–Cunningham law. A large number of observations (Whytlaw-Gray and Patterson, " Smoke," p. 169) were made in this way on droplets of various substances, and it was found that the rate of evaporation is given by the expression $- ds/dt = $ constant, for both small and large droplets; *i.e.*, the rate of change of surface of the droplet on evaporation is independent of its size. This result shows, as might be expected, that diffusion is the determining factor, and that when, as is the case with small droplets, the diffusion gradient is steep, evaporation is accelerated. For instance, droplets of triphenylmethane of about 2×10^{-4} cm. radius were observed to evaporate markedly in 15 minutes, although the vapour pressure of this substance at room temperature is about 2×10^{-5} mm. of mercury. It can be calculated that a particle of this material of radius 1×10^{-5} cm. would disappear in about 5 seconds, provided the same law holds down to very small dimensions.

The coagulation of smokes formed from azobenzene, α-naphthylamine, phenanthrene, and benzil cannot be determined, for although on volatilisation a dense cloud is formed, the particles disappear quickly by evaporation. A steep particulate-volume curve may hence be produced by the joint effect of evaporation and coagulation. Such is the case with mercuric iodide smoke, which gives a steep and straight line for which $K = 2 \cdot 7 \times 10^{-9}$ cm.³/sec., and evaporation may be the explanation of the abnormal value $K = 1 \cdot 4 \times 10^{-9}$ found for homogeneous clouds of benzeneazo-β-naphthol of the usual weight concentration.

To gain a clear impression of the process of coagulation, it is worth while considering the time taken to halve the original number of particles. This is easily found from the formula $\sigma - \sigma_0 = Kt$ by putting $\sigma = 2\sigma_0$, whence $t = \sigma_0/K$ or $1/n_0K$. A smoke of cadmium oxide containing initially 5×10^6 particles per c.c. will have its numbers reduced to a half after coagulating for 250 secs., whilst a 15 mg. stearic acid cloud starting from the same number will take 392 secs. All ordinary smokes, provided their particles are not much smaller than 2×10^{-5} cm. radius, coagulate at rates between these limits. When the initial number is increased by powers of ten, the time taken to halve the number decreases in the same proportion; *e.g.*, a system of cadmium oxide containing 5×10^{10} particles per c.c. will halve its numbers in 0·025 sec., and to reach by coagulation a value of $2 \cdot 5 \times 10^6$, a number 20,000 times smaller, will take only 500 seconds.

It follows, therefore, that when the number concentration is high, coagulation is so rapid that the number per c.c. present after a few minutes is practically independent of the initial number. For instance, using as before the constant for cadmium oxide, *i.e.*, $K = 0 \cdot 80 \times 10^{-9}$ cm.³/sec., whether we start with a system of 5×10^{12} or of 5×10^8 per c.c., the time taken to form by coagulation a system containing $2 \cdot 5 \times 10^6$ per c.c. is nearly the same. This explains why it is that, on forming a smoke from different quantities of material, the number, by the time the cloud is ready to examine, is the same though the average size is different.

Now all smokes, in contradistinction to dusts which arise by true dispersion of some kind or another, are in reality formed by a process of condensation, and the particles grow from molecular dimensions. The coagulation constant for very small particles is, as we

have seen, distinctly greater, so that in the early stages coagulation will proceed faster. Usually, too, the smokes we have used have been formed by diluting rapidly with air the very concentrated smoke first produced, so that the process before dilution must be extremely fast. In the early stages it is certainly incorrect to assume, as in the above calculation, that the value of K remains the same; it is certainly much greater, and the same stage of the process will undoubtedly be attained earlier. The true particulate-volume curve in the first stages is probably of the form shown in Fig. 4, but is too steep to be followed.

When the formation of a smoke is observed carefully inside the cubic-metre chamber, it is easy to see that the vapour arising from the heated boat condenses immediately, either partially or entirely, to smoke before it is mixed by fanning with excess of air. The volume of this smoke cannot be much greater than the volume of the vapour; in the case of 16 mg. of stearic acid, it can hardly exceed 100 c.c. and is probably much less, so that at a maximum it is one ten-thousandth of the volume of the air with which it is subsequently mixed. But it is not possible to make counts until after some five minutes have elapsed, so, supposing that then 5×10^6 particles per c.c. are present, over 10^7 per c.c. must have been in the smoke immediately after dilution, and the number in the smoke arising from the boat before mixing must have been of the order of 10^{11} or 10^{12} per c.c.

FIG. 4.

FIG. 5.

Particulate-volume graph of early stage
of coagulation.

Reproducibility of standard stearic acid
smoke.
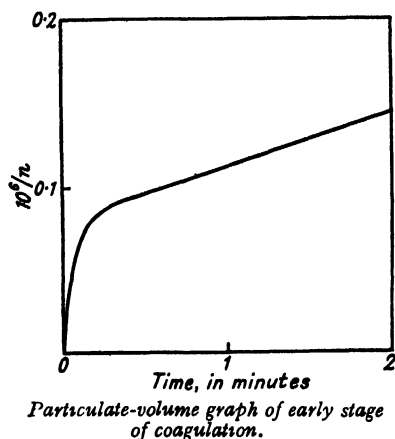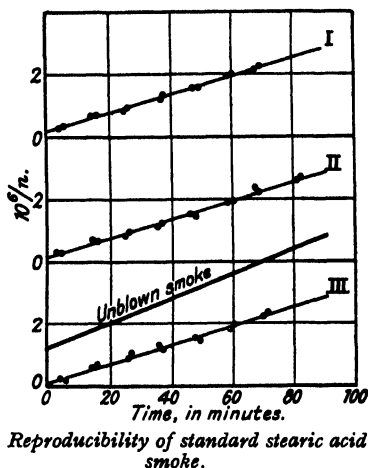
It is evident, then, that in smokes formed in this way, coagulation will proceed to an advanced stage, and on dilution a heterogeneous system will be formed containing a large variety of particles of different sizes. It is easy to see that a difference of a small fraction of a second before mixing may alter considerably the character of a smoke. The difficulty of obtaining by this process of formation, systems which coagulate at the same rate is now explained. For a long time we could not get reproducible results with the same smoke formed under the same conditions until the extreme rapidity of the coagulation process in its early stages was recognised. Clearly, in order to get the same result on successive occasions it is necessary to arrange the initial process so that the smoke is diluted instantly. For substances which volatilise at moderate temperatures this can be achieved by passing a very rapid current of hot, dust-free air over the heated boat from which the material is volatilising. The details and experimental conditions for success by this method have been carefully studied by Patterson and Cawood (*Proc. Roy. Soc.*, 1932, *A*, **186**, 358) for stearic and oleic acids and also for a number of other substances.

Smokes formed in an air blast in this way, which it is convenient to call "blown smokes," invariably coagulate at a slower rate than smokes produced inside the chamber and mixed by means of a fan, and are reproducible to a marked degree. In a recent paper, these authors give examples of fourteen different stearic acid smokes of the same weight con-

centration, in which the constant K varied only from 0·50 to 0·53 × 10⁻⁹ cm.³/sec., and also of thirteen others formed in a much larger chamber (3·3 cu. m.) which gave values ranging between the same extremes. The reproducibility of these smokes is shown in Fig. 5, where the experimental points are given and for comparison an unblown smoke is included. The difference between the blown and the unblown type can only be due to the former being more homogeneous. This is supported by the appearance of the particles in the ultramicroscope, which appear initially of equal brightness and mobility. The use of these blown smokes makes it easier to determine the effect of particle size on coagulation rate. As an example, a series of concordant results obtained with blown smokes of stearic acid of weight concentrations of 10, 15, and 30 mg. may be quoted : the respective K values were 0·56, 0·51, and 0·48 × 10⁻⁹.

As Winkel and Jander have pointed out (*Kolloid-Z.*, 1933, **63**, 5), the conception of homogeneity and heterogeneity in a smoke is purely statistical. No coagulating smoke can be really homogeneous, although at the start it may be nearly so. Its particles may fall within either a narrow or a wide range of sizes according to its past history.

In this sense dusts, in particular, and many industrial smokes are widely heterogeneous, whilst country fogs and clouds approximate to homogeneous systems.

Town fogs are of the heterogeneous type, for the smoke particles of which they are composed coagulate to a considerable extent before they emerge from chimneys and are diluted by the atmosphere. The particles are hygroscopic and readily grow to a comparatively large size, whereupon their opacity is great although the actual number concentration is small. On this account the diminution of fogs by coagulation is slow, although the actual coagulation constant is normal. Experiments made in Leeds show that the number per c.c. in a dense fog is about 1—2 × 10⁵.

The particles are highly charged electrically and contain approximately equal numbers of both signs. To halve by coagulation the number of particles would take about 3½ hours, and about 16 hours would be required to reduce the total to 2·5 × 10⁴, a number comparable with the usual dust content of town air.

A very interesting smoke which approximates to the monodisperse or homogeneous type has recently been discovered and investigated by Jander and Winkel (*loc. cit.*). The system is composed of particles of ferric oxide, and is formed by exposing a mixture of iron pentacarbonyl and air to the action of light of short wave-length, a quick photochemical decomposition producing ferric oxide and carbon monoxide. Since the smoke can be formed by uniform radiation throughout the whole volume and no dilution is necessary, a highly homogeneous system can be obtained. Dr. Cawood and I have recently determined its coagulation constant and have examined the complex particles microscopically; the latter are markedly of chain structure and resemble the complexes of cadmium oxide. As was expected, the particulate-volume curve is straight for a 16 mg. cloud, and shows no sign of the curvature found by Jander and Winkel, which we think was due to an error in counting inherent in the slit ultramicroscope they used. The constant found, *viz.*, 0·66 × 10⁻⁹ cm.³/sec., lies close to that of a 15 mg. ammonium chloride smoke, and is distinctly smaller than the value for cadmium oxide. This is an important piece of evidence, for it is the first measurement made of the constant of a homogeneous smoke forming chain-like complexes : the arc smokes previously examined were probably more or less heterogeneous.

It appears as if the particle structure has no considerable influence on the coagulation rate, for there is no great difference between this smoke and the standard stearic acid which forms compact aggregates. For sols, however, of very long rod-shaped particles, a large increase in coagulation rate has been found (Wiegner and Marshall, *Z. physikal. Chem.*, 1929, **140**, 1).

So far, coagulation has been considered entirely from the experimental standpoint. It remains to be seen whether a theoretical formulation of the process, similar to that derived by Smoluchowski and applied to sols, is possible for smoke systems.

Assuming that the particles are spherical, are all of the same size, and that Brownian motion alone is responsible for their impacts, Smoluchowski deduced the expression $1/n - 1/n_0 = \frac{4}{3} . RTst/\eta N$ for the change with time of the total number of particles in a

sol undergoing quick coagulation. In this formula, n and n_0 have the usual significance, R is the gas constant, T the absolute temperature, N the Avogadro number, η the viscosity of the medium, and s the ratio of the radius of the sphere of influence of the particle to the actual radius.

If it is supposed that the particles only cohere when they hit, i.e., when they approach within two radii, s becomes equal to 2, and the expression becomes $1/n - 1/n_0 = \frac{4}{3} . RTt/\eta N$ which, for any one medium at a constant temperature, is $1/n - 1/n_0 = Kt$, identical in form with that found experimentally for smokes.

The value of K so calculated, however, though in agreement with the experimental data for sols, as the comprehensive investigations of Tuorila (*Koll. Chem. Beih.*, 1926, 22, 192—394) and Wiegner (Wiegner and Tuorila, *Kolloid-Z.*, 1926, 38, 3) have recently shown, diverges considerably for smokes. For instance, using the appropriate value for η for air at 20°, the calculated K value is 0.29×10^{-9} cm.³/sec. instead of 0.51×10^{-9} found experimentally for standard stearic acid smoke.

The above expression is not really applicable to gaseous or aerial systems, for in these media the mean molecular free path is of the same order of magnitude as the particles themselves, and their mobility is greater than it would be were the medium truly homogeneous. In other words, the smoke particles in Brownian motion move through the spaces in the medium, and the simple resistance law of Stokes, $F = 6\pi\eta rv$, no longer expresses their mobility, but must be modified by a correction factor $(1 + Al/r)$. The validity of this correction term, first proposed by Cunningham, has been proved experimentally within wide limits by Millikan. In this expression, $l =$ mean free path, $r =$ radius of particle, and $A =$ constant.

For the simplest case, then, of a truly homogeneous smoke of spherical particles in the initial stage of coagulation, the expression $\dfrac{1}{n} - \dfrac{1}{n_0} = \dfrac{4}{3}\dfrac{RT}{\eta N}\left(1 + \dfrac{Al}{r}\right)t$* should apply.

From the form of the equation, it is evident that K is not a constant but grows smaller as coagulation proceeds and the radius of the average particle increases. The experimentally determined graphs, however, are straight lines within the limits of experimental error except for the case of very small particles, for which there is indication of curvature.

Inserting in the above equation the appropriate numerical values at 20°, i.e., $\frac{4}{3}RT/\eta N = 0.292 \times 10^{-9}$ cm.³/sec. and $Al = 9 \times 10^{-6}$, and taking as the radius of the particle the value calculated from the weight in a standard stearic acid smoke of number concentration of 2×10^6 per c.c. when the density of the particle is assumed to be normal, we get $K = 0.510 \times 10^{-9}$ cm.³/sec., whilst the mean value from a large number of concordant experiments is $K = 0.523 \times 10^{-9}$ cm.³/sec.

This agreement between theory and experiment is to some extent misleading. In reality, the experimental value of K is determined by drawing a mean line through all the experimental points, and what is really wanted for a strict comparison is the K value in the early stages which, if there is a slight curvature, would be different. Patterson and Cawood (*loc. cit.*), who have discussed this question in detail, conclude that actually the two values would agree closely if account could be taken of the size distribution of the smoke, and the true mean radius used to compute K at various stages of coagulation. The mean of these values for K should be truly comparable with the experimental value. At present, the only way of arriving at the size distribution in these smokes is by calculation, using Smoluchowski's equations for the numbers of 1, 2, 3, 4 . . . . . n-fold particles present in a sol after given intervals and applying the result to smokes. This, as the authors point out, must lead to a result which is somewhat inaccurate, but until a method of determining experimentally the size range in smokes is available, it is the only possible approximation.

That there is agreement at all is sufficiently striking considering that the Smoluchowski expression contains no arbitrary constant and depends only on Brownian motion and the theory of diffusion. It is satisfactory, too, to note that only those smokes which approximate to uniformity and the particles of which coagulate to compact aggregates,

* For a derivation of this equation and its application to heterogeneous systems, see " Smoke," pp. 63, 64.

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such as oleic and stearic acids, give a good agreement. Heterogeneous smokes and those composed of chain-like particles coagulate too rapidly. The only case investigated of a smoke coagulating to spheres is that of paraffin oil and perhaps resin. Heavy paraffin oil when dispersed inside the chamber gives a typically heterogeneous smoke and coagulates much at the same rate as ammonium chloride dispersed in a similar manner. When, however, it is produced in a blast of heated air, it coagulates at the same rate as the stearic acid smokes. Unfortunately, the data for this smoke are not sufficiently numerous to allow its constant to be known to the same accuracy as that of stearic acid.

Smoluchowski's theory, which has been shown by many workers to be valid for sols, thus finds strong additional support from work with aerial systems. It is interesting to compare the rates of coagulation of the two classes of system. The following two values of the constants of monodisperse systems in water are taken from the results of Tuorila :

Suspension.	Radius of particle, cm.	Coagulation constant, cm.^{3}/sec. $\times 10^{11}$.
Kaolin	3×10^{-5}	0·53
Coarse gold sol	$9 \cdot 7 \times 10^{-6}$	0·56
Theoretical value at 20°	—	0·52

For comparison the theoretical value calculated from the formula on p. 277 is given. With these may be compared the value $K = 0 \cdot 52 \times 10^{-9}$ cm.^{3}/sec. found for stearic acid smoke; and it is evident that the constant for smokes is about 100 times greater than for sols and aqueous suspensions. There is, however, an important difference between the quick coagulation of sols and suspensions and the coagulation of smokes, for in sols the process is independent of the size of particle, whilst in smokes coagulation increases rapidly when the particle is smaller than 1×10^{-5} cm. radius. Both these deductions from theory have been confirmed experimentally, but from the experimental evidence with very fine smokes it appears as if the calculated values for K are too high. This point would be worth investigating.

Another important effect foreseen by theory is the greater rate of coagulation of hetero-geneous smokes. It is easily shown that the probability of collision between particles of unequal size must be greater than that between those of equal dimensions. The effect is, however, small unless the size difference is great. Smoluchowski assumed in his calcul-ations that the chances of encounter were equal. Whilst this is a close approximation for systems which are uniform at the start, it leads to a coagulation rate which may be much too small when, as in the later stages of coagulation, a large range of sizes is present.

Müller (*Kolloid-Z.*, 1926, **38**, 1) has extended Smoluchowski's equations to include systems which are highly polydisperse, and Tuorila has tested them experimentally for sols and obtained a satisfactory concordance with theory.

When the theory for smokes is examined, it is easy to see that heterogeneity must lead to an increased rate, but it is difficult to apply it quantitatively, and on the experi-mental side the coagulation of mixed systems consisting of particles of different sizes has not been investigated so far.

In view. then of these theoretical considerations and of the experimental evidence, we can form a rough picture of the course of coagulation during the life history of a blown smoke. Any small particles will disappear rapidly from the system, for they will unite with the larger units and with each other at a rate much exceeding the normal.

At a certain stage, depending on the relative dimensions of the units as well as on the actual size of the small ones, a maximum degree of uniformity will be reached, and after-wards the normal rate of coagulation will render the system less and less homogeneous as time goes on. The degree of heterogeneity reached by a homogeneous smoke in the time over which it is usually studied is not great. For example, the number of particles in a stearic acid smoke will have been reduced to one-tenth at the end of an hour, which means that the average radius will be only a little more than twice as great as it was initially, a difference which would produce a very small effect on the coagulation rate. It would be of interest to study the coagulation of smokes over much longer periods.

The expression $K = 4RT(1 + Al/r)/3\eta N$ enables the influence of changes of pressure,

viscosity, and temperature on the coagulation rate of smokes to be predicted. It is evident that in gases of a large mean free path and a low viscosity coagulation should be rapid. Lowering of pressure should produce a change in the same direction, K increasing in proportion with the $(1 + Al/r)$ term, the viscosity remaining constant. A rise in temperature should, however, be partly balanced by the increased viscosity and have only a small effect on K. Up to the present, no smokes formed in gaseous media other than air have been studied. The effect of pressure on the coagulation rate of ferric oxide aerosols produced as described on p. 276 has been investigated by Jander and Winkel (*loc. cit.*), who find that the number of particles remaining after 1 hour in systems of the same initial concentration varies linearly with the pressure. This is not in agreement with the predictions of theory and needs confirmation. It would be interesting if it were established.

An extension of these methods of investigations to coarser systems such as dusts would be of great interest, for in these the size distribution can be measured microscopically with some accuracy, as the researches of Green (*J. Indust. Hyg.*, 1934, **16**, 29) have shown. Also, it appears from his preliminary observations that these suspensions coagulate faster than smokes, which may be due to the larger particles falling past the smaller and so increasing the chances of a collision. This has been proved to be the case for aqueous suspensions by Wiegner and Tuorila (*Koll. Chem. Beih.*, 1927, **24**, 1) in their investigation of what they term " orthokinetic " coagulation.

A factor which so far has not been considered in discussing coagulation in smokes is electrification. The particles in smokes produced at a high temperature, such as arc smokes, smokes from flames, etc., are as might be expected highly charged, though usually the smoke as a whole is electrically neutral. In these, the number of charged particles of opposite sign remains constant for long periods during coagulation, owing probably to the large number of electrons each particle carries and to the rarity of collisions between units carrying equal and opposite charges. Smokes formed by volatilisation at low temperatures and also by many chemical reactions contain at first few charged particles, but as coagulation proceeds the proportion of these increases and may rise in a few hours to 75% of the total. This effect is due to the catching of ions from the surrounding air, and the ions so caught do not easily escape again.

Patterson (*Phil. Mag.*, 1931, **12**, 1175) has shown how the change in the proportion of charged units with time can be calculated from the coagulation constant of the smoke and the rate of formation of ions in the surrounding air. Whether the presence of electrified particles in a smoke influences the rate of coagulation has not been determined. It is, however, certain that the presence of charges produces no very marked effect. Rough experiments on the coagulation rates of charged and uncharged smokes of zinc oxide showed no clear distinction in their behaviour. Similarly, no clear difference could be detected in the coagulation rate of uncharged ammonium chloride and a highly charged smoke of the same material formed in the presence of X-rays. Smokes containing a large percentage of particles charged to one sign can be formed by means of the silent electric discharge, but these in course of time lose their unipolar character and after a few hours contain equal numbers of positive and negative units. It might be expected that coagulation in a unipolar smoke would be arrested or its rate at least diminished. Although experiments have been made on this, the evidence so far is confused and no certain conclusions can be drawn.

It is evident that the coagulation of smoke and other disperse systems in air presents a close analogy to the process of quick coagulation in sols. In both the particles collide as a result of Brownian motion and the agreement between theory and experiment renders it probable that in smokes as in sols every collision between particles is effective.

In aerial systems the greater velocity of the process is a consequence not only of the much smaller viscosity but also of the discontinuous nature of the medium, air, which for the smoke particle of average size is far from homogeneous. As a result, coagulation of particles of radius 1×10^{-5} cm. or 0.1μ is about twice as fast as it would be in a continuous medium of the same viscosity as air, and it increases rapidly as the particle size falls, whilst in sols it is independent of size. At present, on account of the paucity of experimental data a correlation of coagulation velocity and particle size is only possible with

the help of theory. Although there is no doubt whatever that the effect is real, further experimental work would provide an interesting test of current theories.

Another factor which affects the coagulation process in both sols and smokes is the degree of uniformity in size of the particles. Whether it is possible to form a smoke which in this sense is really homogeneous may be questioned, but theoretically it is easy to see that a small degree of heterogeneity must have little effect and experimentally it is found that the more nearly a smoke approaches uniformity the slower it coagulates.

These two effects, the greater probability of encounter (*a*) when the particles are small and (*b*) where they vary considerably in size, determine the course of the coagulation process during the life history of smokes. Initially the so-called coagulation constant *K* is large on account of the small size of the particles; it decreases rapidly at first and afterwards more slowly, but as the smoke becomes heterogeneous the second effect (*b*) becomes operative and tends to make *K* increase again. The result is that these two effects often partially neutralise each other, with the result that *K* found experimentally is a constant and the particulate volume curve is a straight line.

As far as this field has been explored at present no counterpart to the process of slow coagulation in sols has been discovered, nor has any definite indication been found of the possibility of arresting coagulation and obtaining a stable smoke.

In the reverse direction, since, apparently, smoke particles always cohere on impact and do not rebound, there is little possibility of accelerating the coagulation rate except by processes which increase the sphere of influence of the particles, such as turbulence, sound waves, or electrical forces.

Although the investigations described here have thrown some light on the properties of a class of disperse system about which little is known, much remains to be done, and it is hoped that this preliminary survey may attract attention to the importance of further studies in this field.

58. *The Solubility of Non-electrolytes. Part I. The Free Energy of Hydration of Some Aliphatic Alcohols.*

By J. A. V. Butler, C. N. Ramchandani, and D. W. Thomson.

THE factors which determine the free energies of solutions may be divided into two groups : (i) those operating in such dilute solutions that there is no interaction between solute molecules, (ii) additional factors in more concentrated solutions where this interaction cannot be ignored. These factors may be separated thermodynamically by expressing the free energy of a solute by

$$\bar{F} = \bar{F}^\circ + RT \log Nf' \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\bar{F}^\circ$ is taken as a constant for a given solvent and the variation of the free energy with the concentration (in so far as it differs from $\bar{F} = \bar{F}^\circ + RT \log N$) is expressed by means of the activity·coefficient f', which is taken as unity when the molar fraction $N \to 0$. Up to the present, more attention has been given to the variation of the activity coefficients with concentration than to the elucidation of the factors determining $\bar{F}^\circ$. Of the factors determining solubility, the latter is usually the more important term, particularly in the case of slightly soluble substances. Moreover, since this quantity depends only on the interactions between the solute molecule and the solvent molecules in its vicinity, it presents a more favourable case for theoretical interpretation. In this series of papers we propose to determine $\bar{F}^\circ$ for a variety of solutes and solvents, the present paper being concerned with the aliphatic alcohols in aqueous solution.

It is necessary to refer $\bar{F}^\circ$ to some constant standard state for each substance. In a previous investigation (J., 1933, 674) we determined for a number of these alcohols the quantity

$$\bar{F}^\circ - F^\circ{}_2 = RT \log (p/p^\circ N) = RT \log f^\circ \quad . \quad . \quad . \quad . \quad (2)$$

where F°_a is the free energy of the substance as a pure liquid, having the vapour pressure p°, p is its partial pressure over a very dilute solution of molar fraction N, and f° is the activity coefficient in such a solution referred to the pure liquid, in which the value is unity. This quantity is not, however, well adapted for theoretical interpretation, since it involves a consideration of the state of the substance as a pure liquid, itself a complex state. It is preferable to take the gaseous state as the standard of reference. Thus, if F°_g is the molar free energy of a substance in the vapour at unit pressure (1 mm. Hg), its free energy at a pressure p is

$$\bar{F} = F^\circ_g + RT \log p . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

so that if p is the partial pressure of the solute over a solution of molar fraction N, which is so dilute that $f' = 1$, we obtain by equating (1) and (3), the following quantity which may be called the free energy of hydration of the solute;

$$\bar{F}^\circ - F^\circ_g = RT \log (p/N). \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The ratio p/N, which is in effect the limiting value at small concentrations of the distribution ratio of the substance between the vapour and the solvent, may be determined by one of the following two methods according to whether the miscibility is high or not. (1) By direct measurement of the partial vapour pressure of the solute in a sufficiently dilute solution, or by extrapolation from the values of more concentrated solutions. Values for the two lowest normal alcohols can be obtained from the data previously given (*loc. cit.*). In the case of n-propyl and n-butyl alcohols, insufficient points were available for an accurate extrapolation, and measurements of this ratio were made with dilute solutions of these alcohols, and also for *iso*propyl, three isomeric butyl, and four amyl alcohols. (2) When the miscibility is low, the ratio (p/N) for dilute solutions is given by p°/N_s, where p° is the vapour pressure of the pure solute and N_s its molar fraction in the (dilute) saturated solution. This is exact if the solute is a solid, and may be taken as reasonably accurate in the case of liquids of small mutual miscibility; N_s has been determined for the four normal alcohols C_5—C_8. In order to use these values, it was necessary to know the vapour pressures of the alcohols at 25°. We have therefore determined these over a range of temperature, from which an extrapolation to 25° could be made. Since the recorded vapour pressures of alcohols are very incomplete, it appeared to be useful to determine those of other alcohols, of which we had purified specimens.

EXPERIMENTAL.

Determination of the Vapour Pressures.—The method was a modification of the isotensiscope method of Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, **32**, 1412). The liquid was contained in a 5-c.c. bulb with a small manometer attached. This was connected through a ground joint (with mercury seal) to a vertical condenser, and a large reservoir, provided with a mercury manometer and an efficient pump. The small manometer contained some of the bulb liquid, and the method consisted in observing the reservoir pressure and the temperature of the bulb when the levels of liquid in the two arms of the small manometer were the same. The small bulb and manometer were immersed in a well-lagged glycerol-bath provided with an electric heater and a very efficient stirrer. It was found possible by manual handling for one experimenter to keep the temperature of the bulb constant to $\pm 0.01°$ below 100° and to $\pm 0.02°$ above 100°, while the other adjusted the pressure in the reservoir to give equal levels in the small manometer. The thermometers used were calibrated against standards certified by the N.P.L. The barometer was new, and was checked against the readings of the local meteorological station, a correction being made for the difference of altitude. The levels of the large manometer were read with a cathetometer reading to 0.05 mm. The method depends on the bulb being initially free from air. At the beginning of the experiment the pressure in the apparatus was reduced so that vapour from the bulb bubbled through the liquid of the small manometer and carried with it the dissolved air. This was continued until a concordant series of vapour pressures was obtained both at increasing and at decreasing temperatures.

Materials.—The higher alcohols were the specimens used in the solubility determinations. Before use they were dried and redistilled. The other alcohols were the purest B.D.H. prepar-

ations; these were refluxed over lime for 18 hours, and fractionated through a long column. The fractions employed distilled within a range of less than 0·2°. The ranges within which the fractions used were collected are given below, together with other physical constants. The b. p.'s (corr.) were obtained from observations in the vapour-pressure apparatus of the temperature corresponding to atmospheric pressure, with a correction to 760 mm. from the slope of the vapour-pressure curve.

Alcohol.	B. p./mm.	B. p./760 mm.	D_4^{25}.	n_D^{20}.
*iso*Propyl	82·01—82·03°/748·4	82·39°	0·7812$_6$	1·3688$_6$
n-Butyl	117·16—117·26/742·4	117·71	0·8059$_2$	1·3998$_3$
*iso*Butyl	107·87—107·91/767·1	107·89	0·7983$_3$	1·3960$_3$
sec.-Butyl	99·58—99·70/755·3	99·95	0·8029$_9$	1·3984$_6$
tert.-Butyl *	81·77—81·87/733·4	82·75	—	—
n-Amyl	137·1—137·2/747·4	137·75	0·8125$_2$	1·4111$_2$
*iso*Amyl	131·15—131·35/761·2	131·35	0·8102$_2$	1·4096$_4$
sec.-Amyl	120·26—120·29/775·3	119·89	0·8052$_5$	1·4178$_7$
tert.-Amyl	101·98—102·2/768·3	101·9	0·8059$_4$	1·4058$_0$
n-Hexyl	64·4—64·5/9	155·7	0·8183$_5$	1·4182$_7$
n-Heptyl	76·7—76·8/9	175·6	0·8205$_2$	·1·4252$_7$
n-Octyl	89·1—89·2/9	194·5	0·8232$_2$	1·4295$_7$

* M. p. 25·5°.

Results.—The values obtained are given in Table I. Of these, agreement with previously recorded data is shown in four cases, *viz.*, *n*-butyl alcohol (Kahlbaum, *Z. physikal. Chem.*, 1898, **26**, 577); *iso*butyl and *iso*amyl alcohols (Schmidt, *ibid.*, 1891, **8**, 628; Richardson, J., 1886, **49**, 761), and *tert.*-butyl alcohol (Parks and Burton, *J. Amer. Chem. Soc.*, 1928, **50**, 24). The results for *n*-amyl alcohol are not in agreement with those recorded by Grassi (*Nuovo Cim.*, 1888, **23**, 109), while in the remaining six cases no pressures over a range of temperature have been recorded. Table II gives the constants of the extrapolation formula

$$\log_{10}p = A - B/T - C \log_{10}T,$$

which are required to reproduce the experimental figures. The average deviations (%) in either direction between the experimental values and those calculated by this formula are given under Δ, and ΔH_{298}. is the calculated latent heat of vaporisation at 25°. The values for the higher-boiling alcohols at 25°, which are given in parentheses in Table I, were obtained from these formulæ.

TABLE I.

Vapour pressures of aliphatic alcohols (mm. Hg).

T (K).	*n*-Butyl.	*iso*-Butyl.	*sec.*-Butyl.	*tert.*-Butyl.	*n*-Amyl.	*iso*-Amyl.	*sec.*-Amyl.	*tert.*-Amyl.	*n*-Hexyl.	*n*-Heptyl.	*n*-Octyl.
298·13°	6·78	11·56	17·15	(42·41)*	(2·50)	3·11	6·03	16·72	(0·719)	(0·224)	(0·083)
303·15	9·57	16·47	24·54	58·15	—	4·61	8·79	23·30	—	—	—
308·18	13·50	22·39	33·30	78·18	—	6·75	12·44	32·0	—	—	—
323·23	34·45	55·62	80·74	177·8	—	18·09	32·40	77·14	—	—	—
333·27	60·69	95·84	138·4	291·4	26·01	33·78	57·92	129·8	9·75	3·79	1·65
343·45	103·0	159·7	224·1	462·4	46·15	59·27	99·12	211·4	17·74	7·48	3·31
348·58	—	—	—	547·0	—	—	—	—	—	—	—
353·74	168·5	256·4	355·2	705·9	77·74	99·52	161·8	332·8	31·60	14·35	6·68
363·99	266·6	397·8	543·1	—	125·8	160·6	255·5	505·5	54·57	25·73	11·92
374·32	406·3	600·7	—	—	198·0	251·5	390·4	—	90·01	44·12	21·51
383·35	578·6	—	—	—	286·9	361·2	550·2	—	135·1	67·96	33·42
393·71	—	—	—	—	424·1	532·3	—	—	207·2	107·2	54·02
404·04	—	—	—	—	611·9	—	—	—	309·8	163·6	85·43
414·83	—	—	—	—	—	—	—	—	456·8	246·5	132·63
425·93	—	—	—	—	—	—	—	—	659·8	364·5	201·45

* Solid at 25°.

The Partial Pressures of the Alcohols in Dilute Aqueous Solutions.—We used the air-bubbling method previously employed (Butler, Thomson, and Maclennan, *loc. cit.*). In sufficiently dilute solutions, it is, however, unnecessary to determine the total weight of vapour carried over by a measured volume of air. Assuming that Raoult's law ($p_1 = p_1°N_1$) holds for the solvent, the partial pressure of the solute can be determined by the observation of the relative proportions of the solute and solvent in the vapour only. For, if n_1 and n_2 are the relative molar concentrations of the solvent and solute in the condensate of the vapour, and p_2 is the partial pressure of the solute, we have $n_2/n_1 = p_2/p_1°N_1$, from which p_2 can be determined.

TABLE II.

Constants of the extrapolation formula.

Alcohol.	A.	B.	C.	Δ, %.	$\Delta H_{295°}$.
n-Butyl	40·2105	4100	10·35	0·12	12,630
isoButyl	43·5513	4185	11·50	0·3	12,340
sec.-Butyl	43·4800	4110	11·50	0·5	12,000
tert.-Butyl	43·2834	3935	11·50	0·12	11,200
n-Amyl	46·4925	4580	12·42	0·2	13,600
isoAmyl	51·5074	5120	16·10	0·6	13,900
sec.-Amyl	48·4849	4550	13·11	0·6	13,060
tert.-Amyl	47·4492	4280	12·88	0·15	11,960
n-Hexyl	51·0030	5068	13·80	0·4	15,020
n-Heptyl	56·1972	5580	15·41	1·5	16,410
n-Octyl	65·2106	6190	18·40	1·0	17,430

The compositions of the condensates were determined by interferometric methods, at least two reasonably concordant values being obtained in every case. The results are given in Table III, where N is the molar fraction of the solute in the solution, x the composition of the condensate (wt. %) at 25°, and p its partial pressure (in mm. Hg).

TABLE III.

Alcohol.	$N \times 10^2$.	x.	p.	p/N.	Alcohol.	$N \times 10^2$.	x.	p.	p/N.
n-Propyl	0·929	3·66	0·270	291	tert.-Butyl	0·937	7·55	0·471	503
isoPropyl	0·986	4·49	0·334	339	n-Amyl	0·468	4·87*	0·249	532
n-Butyl	0·992	5·81	0·356	359	isoAmyl	0·506	5·83*	0·301	593
isoButyl	1·143	9·00*	0·571	499	sec.-Amyl	0·496	5·98*	0·309	622
sec.-Butyl	0·959	6·68	0·413	431	tert.-Amyl	1·033	11·03*	0·601	582

* In these cases the condensate was in two phases and the composition was determined after dilution with sufficient water to give a homogeneous solution.

The results of the investigation are assembled in Table IV. The distribution ratios (p/N) (col. 4) are those obtained by direct measurement of the partial pressure of very dilute solutions, except in the case of methyl and ethyl alcohols, which are obtained by extrapolation from the values at higher concentrations, and those marked with an asterisk, which are derived from the solubility. The values of $f° = (p/p°N)$ (col. 4) are calculated from cols. 1 and 3. The values for the lower alcohols are somewhat greater than those given in the previous paper, because the present measurements of very dilute solutions show that, in making the extrapolation of $p/p°N$ from $N = 0.01$ to zero concentration, too great an allowance was previously made for the flattening of the curve in dilute solutions.

The accuracy of the vapour-pressure determinations depends on the correctness of the condensate composition. The greatest variations of the latter observed in repeated experiments with the same or similar solutions amounted to about 10% but in most cases, particularly when

TABLE IV.

Distribution ratios (p/N) of aliphatic alcohols between the vapour and dilute aqueous solutions at 25°, and related quantities.

Alcohol.	$p°$.	$1/N_s$.	p/N.	$p/p°N$.	$RT \log p/N$.
Methyl	122·2	—	184	1·51	3090
Ethyl	59·0	—	218	3·69	3190
n-Propyl	20·1	—	291	14·4	3380
isoPropyl	44·0	—	339	7·7	3450
n-Butyl	6·78	53·1	360 *	—	—
	—	—	359	52·9	3490
isoButyl	11·56	—	·499	43·2	3680
sec.-Butyl	17·15	—	431	25·1	3590
tert.-Butyl	42·41	—	503	11·8	3690
n-Amyl	2·50	219	547 *	—	—
	—	—	532	214	3730
isoAmyl	3·11	—	593	191	3784
sec.-Amyl	6·03	—	622	103	3812
tert.-Amyl	16·72	—	582	35	3773
n-Hexyl	0·719	903	649 *	903 *	3840 *
n-Heptyl	0·224	3,560	798 *	3,560 *	3960 *
n-Octyl	0·083	12,300	1020 *	12,300 *	4110 *

dilution of the condensate was unnecessary, a much smaller variation was obtained. An uncertainty of 5% in the partial pressure corresponds to about ± 30 cals. in $\bar{F}^\circ - F^\circ_g$. Account being taken of the numerous instrumental factors which enter into the determinations, an error of ± 40 cals. may be allowed in individual cases.

<div align="center">DISCUSSION.</div>

It was shown in the previous investigation that in the series of normal aliphatic alcohols the quantity $\bar{F}^\circ - F_2^\circ = RT \log (p/p^\circ N)$ increases by an approximately constant increment for each additional methylene group. That a large part of this increment is due to the factor p° can be seen from Fig. 1, where the differences of the values of $-RT \log p^\circ$ and of $RT \log (p/p^\circ N)$ from the values of methyl alcohol are plotted for the normal alcohols against the number of carbon atoms. The average increment of $RT \log (p/p^\circ N)$ between C_2 and C_8 is about 800 cals., while the average increment of $-RT \log p^\circ$ is 640 cals., leaving about 160 cals. for the increment of $RT \log p/N$. The experimental values of the latter are shown on a larger scale in Fig. 2. The first interval between C_1 and C_2 is abnormally small, but between C_2 and C_8 the average increment is 165 cals. Since this quantity depends only on the interaction of the isolated alcohol molecule with water, it is clear that each methylene group of the normal alcohols makes a definite contribution to the free energy of this interaction. Although none of the values deviates from the line representing the average increment by more than the possible error, the alcohols above C_5 taken as a group show a somewhat smaller average increment than those below. This might possibly be due to the completion of a ring at this point, but the difference is not very great and the accuracy at present obtainable is not sufficient to make it possible to decide if this effect is real.

The differences of p/N between the isomeric alcohols are not greater in some cases than the possible experimental error of individual determinations. Nevertheless, certain regularities can be detected, as can be seen from the differences of $\bar{F}^\circ - F^\circ_g$ shown in the following scheme.
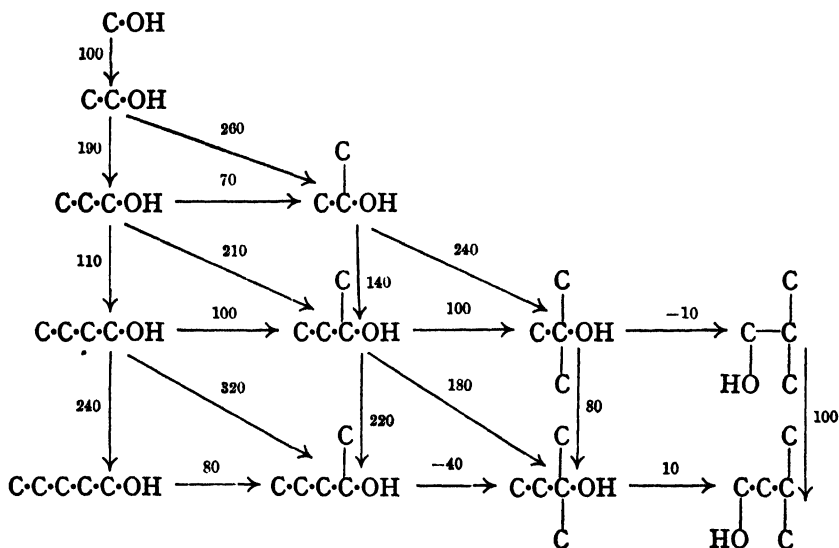
In the alcohols in which the carbon atoms are arranged in a straight chain, the displacement of the hydroxyl group from the terminal carbon to the second (giving a secondary alcohol) causes an increase in $\bar{F}^\circ - F^\circ_g$ of about 100 cals.; *i.e.*, although the addition of a methylene group at the end of a straight chain gives an average increment of 165 cals., yet its addition to the α-carbon atom gives an increment of about 260 cals. A further

increment of the same magnitude is observed when a second methylene group is added in the α-position, giving a tertiary alcohol.

FIG. 1.

FIG. 2.

RT *log* (p/p°N) *and* — RT *log* p° *for the normal aliphatic alcohols.*

Free energies of hydration of aliphatic alcohols (lower series, normal primary alcohols; upper series, secondary alcohols).
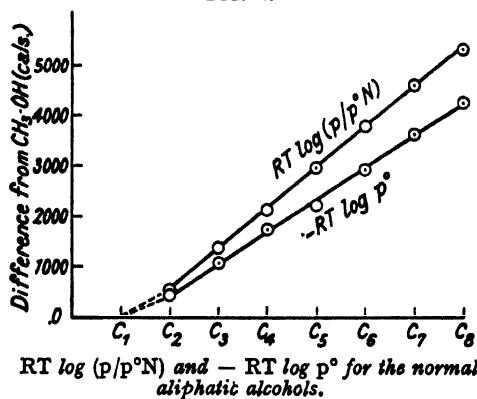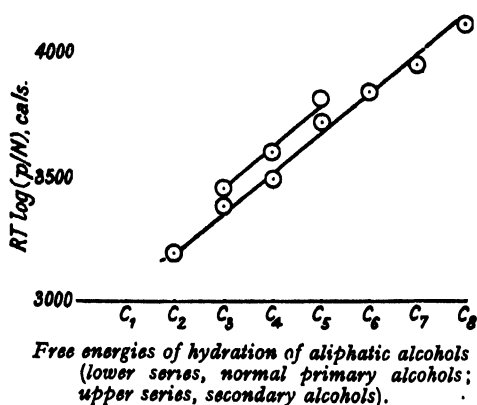
The alcohols with a branched carbon-chain form a group by themselves. The two butyl alcohols having the nucleus (a), Fig. 3, and the two amyl alcohols with the nucleus (b) have nearly the same value of p/N, *i.e.*, in both cases it appears to be immaterial to which carbon atom the hydroxyl group is attached. This can be understood when the spatial arrangement of the carbon atoms in these compounds is taken into account : those in the group (a) are arranged in a pyramid, and it can be seen that a hydroxyl group attached to any one of the carbon atoms is somewhat similarly related to the other three. Similarly, in group (b), the three carbons attached to one carbon atom form a pyramid, while the fourth has freedom of movement, but in aqueous solution its position of minimum energy is under the pyramid, forming a somewhat asymmetric hexahedron. A hydroxyl group attached to either of these carbon atoms will now be somewhat similarly related to the others, irrespective of its position.

FIG. 3.

(a)   (b)

The origin of these effects will be discussed in another paper.
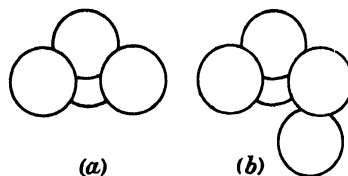
SUMMARY.

1. Measurements have been made of (1) the vapour pressures of eleven aliphatic alcohols over a range of temperature; (2) the partial vapour pressures in very dilute aqueous solution ($N = ca.$ 10^{-3}) of ten aliphatic alcohols at 25°.

2. From these measurements, together with data previously published, we obtain values of the free energy of hydration ($\bar{F}° - F°_g = RT \log p/N$) at 25° of the normal alcohols from C_1 to C_8, of *iso*propyl, three isomeric butyl, and three isomeric amyl alcohols.

3. It is shown that in the series of normal alcohols, of the increment of 800 cals. for each additional methylene group previously found in the quantity $RT \log (p/p°N)$, ($p/p°N$ being the activity coefficient of the alcohol in dilute aqueous solution referred to the pure liquid), about 640 cals. is accounted for by the variation of $RT \log p°$, while the increment of $RT \log (p/N)$ is about 160 cals.

4. The isomeric alcohols show small, but apparently significant, differences the nature of which is discussed.

59. *The Preparation of Diazomethane and its Homologues.*

By DONALD W. ADAMSON and J. KENNER.

FURTHER experience of the method of preparing diazomethane previously described (Jones and Kenner, J., 1933, 363) revealed certain defects. These have now been remedied, and the applicability of the method to homologues and other derivatives of methylamine has been examined.

In one or two instances, large batches of freshly prepared nitroso-β-methylamino*iso*butyl methyl ketone suddenly underwent exothermic decomposition during the preliminary distillation. Since no such difficulty was encountered in redistillation of once distilled material, the decomposition was probably due to the presence of small amounts of basic substance, *e.g.*, either methylamine or its additive compound with mesityl oxide; it has been obviated by use of acetic in place of hydrochloric acid for preparation of the nitroso-derivative. As a further safeguard, the material is run continuously into the small distillation flask at a rate corresponding to that of evaporation. The product is quite stable when preserved in brown bottles.

A more subtle point was involved in a considerable reduction of the yield of diazomethane when large amounts of material were employed. This difficulty, which is also met in using the nitrosourethane method (compare Auwers and König, *Annalen*, 1932, 496, 42, footnote), is due in our case to gradual volatilisation of *iso*propyl alcohol as the diazo-compound is removed by distillation in ether, and is therefore easily overcome. As the equation shows, proton as well as alkoxide anion is essential to the reaction :

$$\begin{array}{c} \overset{\displaystyle \nearrow \overset{-}{O}Pr^{\beta}}{Me_2C\cdot CH_2\cdot COMe} \\ \underset{\displaystyle Me\overset{+}{N}\cdot NO \longleftarrow \overset{+}{H}}{} \end{array} \longrightarrow \quad \begin{array}{c} Me_2C\text{:}CH\cdot COMe + Pr^{\beta}OH \\ + \ MeN\text{:}NOH \end{array}$$
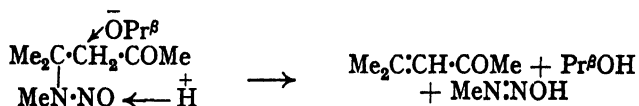
The point is clearly illustrated by the stability of the nitroso-compound, in warm absolute ethereal solution, towards anhydrous potassium carbonate. Diazohydrocarbon is, however, at once evolved if alcohol is added to the mixture, though not in as satisfactory a yield as under our standard conditions.

Subject to these precautions the method would seem to be greatly superior in respect of yield and convenience to current procedure, and we have also successfully applied it to a considerable range of amines, as will be seen from the following table :

" Alkyl " group.	Yield of diazo-derivative, %.	A.	" Alkyl " group.	Yield of diazo-derivative, %.	A.	" Alkyl " group.	Yield of diazo-derivative, %.	A.
Me............	69·0	(7)	n-C$_5$H$_{11}$	33	(35)	CHMe:CH·CH$_2$ ...	24	(20)
Et	50·4	(10)	n-C$_6$H$_{13}$	23	(50)	Furfuryl		
n-Pr	44	(10)	n-C$_7$H$_{15}$	17	(175)	(C$_4$H$_3$O·CH$_2$) ...	12	(175)
n-Bu	41	(20)	n-C$_8$H$_{17}$	16	(175)	(CH$_3$)$_3$CH	0	(—)
*iso*Bu	34	(20)	CH$_2$:CH·CH$_2$	40·5	(10)	(CH$_3$)$_2$CH·CH$_2$ ...	0	(—)

Nirdlinger and Acree (*Amer. Chem. J.*, 1910, 43, 380) mention without any detail the use of solutions of diazopropane and diazobutane (compare also Werner, J., 1919, 115, 1101), and Staudinger has described the preparation of diazo*iso*propane from acetonehydrazone (*Ber.*, 1916, 49, 1885). Apart from these, and diazo-methane and -ethane, the various diazo-compounds seem not to have been previously prepared. The general reaction is obviously applicable to still higher aliphatic amines than those shown, provided the corresponding nitroso-compounds can be distilled below about 180°, which appears to be the extreme temperature they will withstand without decomposition. The rapid rise in boiling point of the diazo-compounds with increase in molecular weight (compare Staudinger, *loc. cit.*) correspondingly hinders their volatilisation in ether, and so not only prolongs the operation but involves their preparation in comparatively dilute solution. The figures in parentheses in the above table (col. *A*) show the volumes of ether (c.c.) required for the complete distillation of the diazohydrocarbon generated in each case from
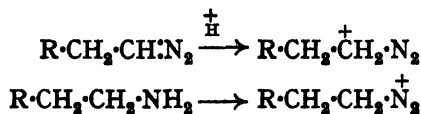
1 gram of nitroso-derivative. This difficulty can be met to some extent by use of *iso*propyl ether, but, on the other hand, it is not practicable to concentrate an ethereal solution by fractional distillation through, for example, a Widmer column. An experiment on these lines with a solution of diazo-octane resulted in decomposition of the diazohydrocarbon, and this instability is obviously partly responsible for the diminution in yield with increase in molecular weight. Staudinger has shown that diazo*iso*propane readily decomposes with formation of dimethylketazine (*loc. cit.*).

The diazohydrocarbons were estimated and characterised by conversion into the corresponding *p*-nitrobenzoates or 3 : 5-dinitrobenzoates, and the following table shows a comparison of melting points with those of specimens prepared by interaction of acid chloride and alcohol (compare Buchner and Meisenheimer, *Ber.*, 1905, **38**, 624), or as recorded by Henstock in connexion with his modification of the Schotten–Baumann method (*J.*, 1933, 216).

	p-Nitrobenzoates.				3 : 5-Dinitrobenzoates.		
Ester.	From diazo-compound.	Buchner–Meisenheimer.	Hen-stock.		Ester.	From diazo-compound.	Buchner–Meisen-heimer.
Me	95·5°	95·5°	96°		n-C_5H_{11}	46·0°	45·5°
Et	56·0	56·0	57		n-C_6H_{13}	58·2	58·5
n-Pr	35—35·5	35·0	32		n-C_7H_{15}	46	46·0
		(b. p. 114/0·05 mm.)			n-C_8H_{17}	58·5	60·5
*iso*Pr	—	110·5	55·5		CHMe:CH·CH₂	50—51	—
		(b. p. 109/0·05 mm.)			Furfuryl		
n-Bu	35·5	35·2	35		(C_4H_3O·CH₂)	84—86	—
*iso*Bu	68·5—69	68·5	67				
n-C_5H_{11}	8½—10½	6½—8½	54				
		(b. p. 133/0·095 mm.)					
CH₂:CH·CH₂	28	28	—				

The agreement between the diazo- and the Buchner–Meisenheimer products is good, but there are striking discrepancies between the data for these and those of Henstock. A repetition of Henstock's work with *iso*propyl alcohol yielded a crude product, m. p. 54—78°, from which the pure product, m. p. 109—110·5°, was ultimately obtained by crystallisation from light petroleum. Henstock used alcohol as a solvent, and it seems significant that two of his discordant values agree with those of the ethyl ester. It is possible that a tendency to reduction of the nitro-group is an inherent difficulty in applying the Schotten–Baumann method to nitrobenzoyl chlorides and alcohols, because in our experience coloured impurities accompany the crude nitrobenzoates so obtained.

Since the use of the higher diazohydrocarbons for esterification or similar purposes involves in the first place reaction with proton, a complex kation should result which is closely comparable with that postulated as the cause of the Wagner–Meerwein change, *e.g.*, in the case of primary amines (compare Adamson and Kenner, *J.*, 1934, 838),

$$R·CH_2·CH:N_2 \overset{\overset{+}{H}}{\longrightarrow} R·CH_2·\overset{+}{C}H_2·N_2$$

$$R·CH_2·CH_2·NH_2 \longrightarrow R·CH_2·CH_2·\overset{+}{N}_2$$

Since *iso*propyl alcohol is produced from *n*-propylamine, it was necessary to determine whether any *iso*propyl ester accompanied the *n*-propyl ester obtained from diazopropane. This was carefully investigated in the cases of the benzoate, the nitrobenzoate, and the iodide prepared from it, but in each instance no *iso*propyl derivative was detected. This is in agreement with the view that decomposition of the diazonium ion depends on attack by anion, *e.g.*, hydroxyl, in the α- or β-position to the diazonium group simultaneously with, and not subsequently to, the separation of nitrogen.

Reference was made in the previous paper to the use of our nitroso-compounds for the alkylation of phenols directly and without preliminary preparation of the corresponding diazohydrocarbon. Since then a process has been described which was devised by Meerwein for the preparation of methyl ethers by the use of nitrosomethylurethane in alcoholic solution in presence of weak bases, *e.g.*, solid potassium carbonate (Schering–Kahlbaum

A.-G., D.R.-P. 579,309). We have now applied this process to β-naphthol and some of the nitrosoalkylamino*iso*butyl methyl ketones with the results summarised :

" Alkyl."	Duration of experiment.	Yield, %.	M. p. of β-naphthyl ether obtained.
Methyl	20 hrs.	70	73°
Ethyl	20 ,,	35	35—36
n-Propyl	20 ,,	34	39—40
*cyclo*Propylmethyl	20 ,,	20	74
Furfuryl	4 days	38·5	oil

Again in the case of the propyl derivative, homogeneity of the product was confirmed, this time by identity of the picrates obtained from the recrystallised ether and from the mother-liquors. The yield of furfuryl ether is three times that of the diazo-compound already recorded, and the result in the case of the *cyclo*propylmethyl ether is even more striking. When account is also taken of the fact that alkylation occurs at the ordinary temperature, whereas diazohydrocarbon formation only takes place at 60—70°, the possibility has to be considered that alkylation may be alternative to diazohydrocarbon formation, just as dealkylation of a quaternary ammonium salt is alternative to olefin formation. The different result could be attributed to the fact that β-naphthoxy-ions enter into co-valent combination with alkyl more readily than with hydrogen :

$$Me_2\overset{|}{C}\cdot CH_2\cdot COMe \longrightarrow Me_2\overset{|}{C}\cdot CH_2\cdot COMe \longrightarrow Me_2C\overset{+}{:}CH\cdot COMe$$
$$C_{10}H_7\bar{O} \longrightarrow R\cdot N\cdot NO \qquad\qquad C_{10}H_7\cdot OR + N\overset{..}{:}NO' \qquad\qquad N_2 + OH'$$
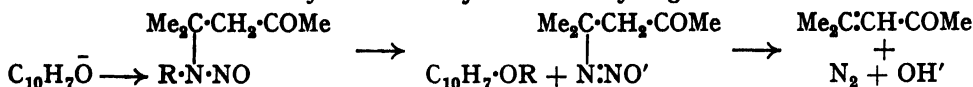
As might be anticipated, vinyldiazomethane (I) is more highly coloured than its analogues derived from saturated amines, and moreover gradually loses its colour owing to formation of pyrazole :

$$(I.) \quad CH_2\overset{..}{:}CH\cdot CH\overset{..}{:}N_2 \longrightarrow$$
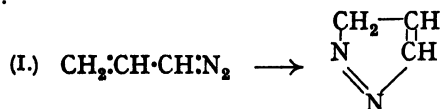
This interesting reaction requires about 36 hours for completion in 0·5% ethereal solution at the ordinary temperature in daylight, but is sensitive to light. Our preliminary measurements under constant illumination have shown the reaction to be accurately unimolecular. The methyl homologue, derived from crotonylamine, is more intensely coloured, and also much more stable. In both instances, reaction with benzoic acid is very much slower than in the cases of the saturated derivatives.

EXPERIMENTAL.

Preparation of Nitroso-ketones.—A solution of sodium nitrite (2 mols.) in the minimum amount of water was added to the product of mixing mesityl oxide (1 mol.) with a primary amine (1 mol.) (compare Jones and Kenner, *loc. cit.*) after neutralisation with glacial acetic acid. Glacial acetic acid (1 mol.) was then added, and the mixture left for 2 hours, ice-cooling being applied if necessary to check too vigorous a reaction. An ethereal extract of the nitroso-compound was washed twice with dilute acetic acid and then with water, and dried over sodium sulphate. Ether having been removed at as low a temperature as possible, the residual nitroso-derivative was distilled under reduced pressure from a small Claisen flask, into the side of which a dropping-funnel had been fused to permit of continuous addition of the crude material. Further distillation of the higher homologues was necessary to remove the small quantities of olefin or alcohol which accompany the crude nitroso-derivative. The following table includes revised boiling points of the compounds previously described :

" Alkyl " group.	B. p./ mm.	N, found, %.	N, required, %.	Yield, %.	" Alkyl " group.	B. p./ mm.	N, found, %.	N, required, %.	Yield, %.
Me	111°/0·5	—	—	67	*n*-C₇H₁₅	156°/0·8	11·6	11·6	60
Et	124/0·7	—	—	72	*n*-C₈H₁₇	151/0·2	11·0	10·9	72
n-Pr	121/0·5	—	—	73	(CH₃)₂CH·CH₂	136/0·7	14·1	14·1	56
*iso*Pr	120/0·7	15·2	15·0	20·4	(CH₃)₃CH	177/0·8	14·3	14·1	35
n-Bu	127/0·6	—	—	70	Furfuryl	158/0·8	12·4	12·5	40·2
*iso*Bu	133/0·7	14·0	14·0	50·4	CH₂:CH·CH₂	117/0·4	15·3	15·2	64
n-C₅H₁₁	154/0·8	—	—	59	CHMe:CH·CH₂	123/0·14	14·2	14·1	65
n-C₆H₁₃	160/0·6	12·0	12·3	60					

Preparation of Diazohydrocarbons.—Experiments by E. C. S. Jones on the scale and lines of those previously described had shown that satisfactory yields of homologues of diazomethane could be obtained, but his results could not be reproduced on the larger scale, even in the case of diazomethane itself, until the general procedure below was evolved and employed in an apparatus consisting of a 20-c.c. Claisen flask carrying a tap funnel and connected to a condenser. The latter was fitted with an adapter dipping below ether (5 c.c.) in a receiver cooled by ice. A solution of the nitrosomethylamino-ketone (4 g.) in absolute ether (30 c.c.) and *iso*propyl alcohol (3 c.c.) was added drop by drop to a 1% solution of sodium in *iso*propyl alcohol (5 c.c.) at 76—80° at a rate equivalent to that of distillation. At an appropriate point in the operation a further quantity of sodium *iso*propoxide solution (4 c.c.) was added. Finally, absolute ether (ca. 5 c.c.) was added until the distillate was no longer coloured. In this way diazomethane (0·7 g.) was prepared in 20 minutes, and larger quantities were prepared as satisfactorily in separate batches as in one larger one. For the homologues, a longer period and a larger supplementary quantity of ether were required owing to the higher b. p.'s of the diazo-compounds. In such cases *iso*butyl alcohol was frequently used in place of *iso*propyl alcohol owing to its higher b. p. and the fact that it dissolves a quantity of its sodium derivative about five times greater than its lower homologue does. Very poor results were obtained by use of *sec.*-octyl alcohol or glycol. The yields were determined by titration as before and are recorded in the introduction.

Of the esters mentioned in the table, the following are new : n-*amyl* p-*nitrobenzoate*, b. p. 133°/0·1 mm. (Found : N, 6·2. $C_{12}H_{15}O_4N$ requires N, 5·9%); *crotonyl* 3 : 5-*dinitrobenzoate* (Found : N, 10·8. $C_{11}H_{10}O_6N_2$ requires N, 10·5%); *furfuryl* 3 : 5-*dinitrobenzoate* (Found : N, 9·6. $C_{12}H_8O_7N_2$ requires N, 9·6%).

Etherification of β-Naphthol.—Equimolecular proportions of β-naphthol and nitroso-ketone were stirred at the ordinary temperature in absolute alcoholic solution (1500 c.c. per g.-mol.) with anhydrous potassium carbonate until evolution of nitrogen had ceased. Alcohol and mesityl oxide having been removed from the filtered solution by evaporation under reduced pressure, the ethereal solution of the residue was washed with dilute alkali, dried, and evaporated. The table given in the introduction summarises the results obtained.

From a similar experiment in which the quantity of methylnitroso-ketone (1·33 mols.) corresponded to the yield of diazomethane already recorded, the yield of methyl ether was 85%.

Naphthyl n-propyl ether furnished a picrate, m. p. 80—81° (Found : N, 10·1. Calc. for $C_{19}H_{17}O_8N_3$: N, 10·1%), and no sign of any isomeride was detected, although Bodroux (*Compt. rend.*, 1898, **126**, 840) recorded 75° as the melting point of the picrate, and 92° as that of the picrate of β-naphthyl *iso*propyl ether.

Pyrazole from Vinyldiazomethane.—The deep red ethereal solution (75 c.c.) from the alkyl-nitroso-ketone (1·6 g.) became colourless after 36 hours at the ordinary temperature, and on evaporation furnished a crystalline residue (0·24 g.), m. p. 67°, which, recrystallised from light petroleum, gave needles, m. p. 69·5°. It did not depress the m. p. of pyrazole prepared by Balbiano's method (*Ber.*, 1890, **23**, 1105). A boiling *iso*propyl ethereal solution of the diazo-compound became colourless within a few minutes.

A quantitative study of the change was made by irradiating an ethereal solution (0·102%) with light from a 60 candle power Osram lamp from a distance of 10 cm., and measuring the Bunsen extinction coefficient at 5140 Å. (where least absorption occurred) in a Hilger Nutting spectrophotometer every ¼ hour. The following readings were obtained, and conform closely to a linear relationship :

Time (hrs.)	0	0·5	1	1·5	2	2·5	3	3·5	4
Coefficient	19·4	17·2	15·0	12·6	10·6	8·6	6·4	4·2	2·4

An ethereal solution of propenyldiazomethane (0·05%) was deeper red than that of vinyl-diazomethane and was only completely decolorised after 14 days at the ordinary temperature : a boiling ethereal solution lost its colour in 2 hours. The product was an oil and on account of the small quantity available was not definitely identified with 3-methylpyrazole, which is also an oil (Knorr and Macdonald, *Annalen*, 1894, **279**, 217).

THE COLLEGE OF TECHNOLOGY, MANCHESTER.

60. *New Derivatives of* p-*Arsanilic Acid. Part VI.* p-*Arsonopimelanilic and* p-*Arsonosuberanilic Acids and Related Compounds.*

By GILBERT T. MORGAN and ERIC WALTON.

PIMELYL and suberyl derivatives of *p*-arsanilic acid have been prepared by condensing the *acid chlorides* of methyl hydrogen pimelate and methyl hydrogen suberate respectively with atoxyl. The products—*methyl* p-*arsonopimelanilate* (I; $n = 5$, $R_1 = $ Me) and *methyl* p-*arsonosuberanilate* (I; $n = 6$, $R_1 = $ Me)—were treated with various amines to give amides of type II ($n = 5$ and 6).

$$H_2O_3As \langle \quad \rangle NH \cdot CO \cdot [CH_2]_n \cdot CO \cdot OR_1 \qquad H_2O_3As \langle \quad \rangle NH \cdot CO \cdot [CH_2]_n \cdot CO \cdot NR_2R_3$$

$$\text{(I.)} \qquad\qquad\qquad\qquad\qquad\qquad \text{(II.)}$$
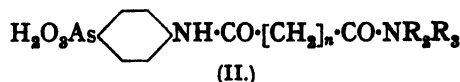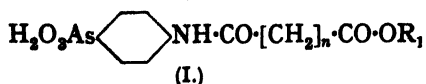
In order to purify the amides of the lower series (II; $n = 1, 2, 3$, etc.) it was usually only necessary to isolate them by acidification and recrystallise them from water. In the higher series ($n = 5, 6$, etc.), however, this procedure was often found inadequate, owing mainly to considerable hydrolysis. The amides of the pimelyl series had usually to be purified by alcoholic precipitation of by-products, chiefly p-*arsonopimelanilic acid* (I; $n = 5$, $R_1 = $ H), in the form of their sodium salts. In the suberyl series, the sodium salts of the amides, owing to diminished solubility, could be purified by simple crystallisation from water.

Suberyl (II; $n = 6$) and adipyl (II; $n = 4$) derivatives show similar tendencies to hydrolyse readily to p-*arsonosuberanilic acid* and p-*arsonoadipanilic acid* respectively.

These amides have all been tested against experimental trypanosomiasis by Professor Warrington Yorke, F.R.S., and collaborators, with results in summary as follows :

Sodium salts.	M.L.D.	M.C.D.	C.R.	Sodium salts.	M.L.D.	M.C.D.	C.R.
Pimelyl series (I and II; $n = 5$) :				*Suberyl series* (I and II; $n = 6$) :			
Ethyl ester	15	—	<1	Ethyl ester	25	12·5	2
Methyl ester	25	—	<1	Methyl ester	25	>25	<1
Carboxylic acid	not examined			Carboxylic acid	50	inactive	
Amide	90	20	>4	Amide	50	12·5	4
Methylamide	50	12·5	4	Methylamide	25	12·5	2
Dimethylamide	100	50	2	Dimethylamide	>50	10	>5
Ethylamide	100	50	2	Ethylamide	25	6·25	4
n-Propylamide	100	50	2	n-Propylamide	not prepared		
Pimelanilide-*pp'*-di-arsonic acid	12·5	—	<1	Suberanilide-*pp'*-di-arsonic acid	10	inactive	

M.L.D. = minimum lethal dose, M.C.D. = minimum curative dose (both as mg. per 20 g. of mouse). C.R. = curative ratio.

These data indicate that trypanocidal power is now diminishing with increasing values of *n* (II). In fact, the maximum activity was apparently attained in the series where $n = 2$ and 3 respectively (Part I, J., 1931, 615; Part III, J., 1932, 276).

Sodium succinanilomethylamide-*p*-arsonate (II; $n = 2$; R_2, $R_3 = $ H, Me), a highly active substance and one of the most readily prepared compounds in these lower series, is now undergoing clinical trial against both neurosyphilis and sleeping sickness.

EXPERIMENTAL.

Pimelyl Derivatives.

Methyl Hydrogen Pimelate and its Acid Chloride.—Methyl pimelate (20—22 g., b. p. 130—135°/17 mm.) was prepared from salicylic acid (25 g.) by a modification of the method recorded in " Organic Syntheses," XI, 42, whereby drainage of the crude product on a Buchner funnel and porous plate was obviated.

Methyl hydrogen pimelate, prepared from the dimethyl ester by partial hydrolysis according to Blaise and Koehler's method (*Bull. Soc. chim.*, 1910, **7**, 215), boiled at 181—182°/18 mm. (yields from 42 g. of methyl pimelate : methyl hydrogen pimelate, 20 g.; pimelic acid, 4 g.; recovered methyl pimelate, 10 g.).

A mixture of methyl hydrogen pimelate (11·7 g.) and thionyl chloride (8 c.c.), after 24 hours at 20° and 4 hours at 70°, gave the *acid chloride*, b. p. 135—136°/17 mm., in theoretical yield (Found : Cl, 18·6. $C_8H_{13}O_3Cl$ requires Cl, 18·4%).

Ethyl hydrogen pimelate and its acid chloride were also prepared in improved yield by these methods.

Methyl p-Arsonopimelanilate (I; $n = 5$, $R_1 = Me$).—Atoxyl (1 g.) in *N*-sodium hydroxide (4 c.c.) was well shaken with the acid chloride (0·5 c.c.) of methyl hydrogen pimelate, and the clear solution poured into an excess of cold dilute hydrochloric acid. The precipitated *methyl p-arsonopimelanilate* crystallised from water in small rectangular prisms, readily soluble in alcohol (yield, 12 g. from 30 g. of atoxyl) (Found : As, 20·2. $C_{14}H_{20}O_6NAs$ requires As, 20·1%). The *sodium* salt separated from dilute ethyl alcohol in minute leaflets, p_H 7·5 (Found : As, 17·9. $C_{14}H_{19}O_6NAsNa,H_2O$ requires As, 18·1%).

Ethyl p-arsonopimelanilate (I; $n = 5$, $R_1 = Et$), prepared in a similar manner from the acid chloride of ethyl hydrogen pimelate, crystallised from water in flattened prisms, readily soluble in warm alcohol (yield, 7 g. from 30 g. of atoxyl) (Found : As, 19·6. $C_{15}H_{22}O_6NAs$ requires As, 19·4%). The *sodium* salt was prepared by evaporation of its aqueous solution, p_H 7·5 (Found : As, 18·4. $C_{15}H_{21}O_6NAsNa$ requires As, 18·3%).

p-Arsonopimelanilic acid (I; $n = 5$, $R_1 = H$), obtained by hydrolysis of the above esters, crystallised from water in striated needles, soluble in warm alcohol (Found : As, 21·0. $C_{13}H_{18}O_6NAs$ requires As, 20·9%).

p-Dichloroarsinopimelanilic acid, from the above acid by reduction with sulphur dioxide and iodine (trace) in concentrated hydrochloric acid, crystallised from benzene in needles, m. p. 114—116°, but gave very low figures for chlorine (Found : Cl, 15·3. $C_{13}H_{16}O_3NCl_2As$ requires Cl, 18·7%). Hydrolysis gave *p-oxyarsinopimelanilic acid*, an amorphous solid, only sparingly soluble in water (Found : As, 23·2. $C_{13}H_{16}O_4NAs$ requires As, 23·1%).

Pimelanilamide-p-arsonic Acid (II; $n = 5$; $R_2, R_3 = H, H$).—The methyl ester (I) (6·3 g.) and concentrated aqueous ammonia (15 c.c.) were heated in a sealed tube for 24 hours at 75°. The crude amide, obtained by removal of the ammonia and acidification, was dissolved in 0·5*N*-caustic soda to p_H 5·5. Ethyl alcohol was then added till milky, and, after boiling, the solution was filtered and evaporated to dryness. Repetition of this process gave a *sodium* salt (2 g.), p_H 5·5 (Found : hydrolysable N, 3·4. $C_{13}H_{18}O_5N_2AsNa,2H_2O$ requires hydrolysable N, 3·4%). *Pimelanilamide-p-arsonic acid*, from this sodium salt, crystallised from water in needles, which, on drying, were suddenly transformed into very loosely packed, rectangular plates, sparingly soluble in alcohol (Found : hydrolysable N, 3·6. $C_{13}H_{19}O_5N_2As$ requires hydrolysable N, 3·9%).

Pimelanilomethylamide-p-arsonic Acid (II; $n = 5$; $R_2, R_3 = H, Me$).—The ethyl ester (I) (2 g.) and 33% aqueous methylamine (4 c.c.), after 2 days at room temperature, followed by evaporation, gave the *methylamine* salt of the *methylamide* (Found : hydrolysable N, 6·6. $C_{15}H_{26}O_5N_3As$ requires hydrolysable N, 7·0%). *Pimelanilomethylamide-p-arsonic acid*, from this salt, crystallised from hot water in minute prisms (1·5 g.), sparingly soluble in alcohol (Found : hydrolysable N, 3·8. $C_{14}H_{21}O_5N_2As$ requires hydrolysable N, 3·8%).

The *sodium* salt crystallised from dilute alcohol in flattened needles, p_H 7·5 (Found : hydrolysable N, 3·25. $C_{14}H_{20}O_5N_2AsNa,2H_2O$ requires hydrolysable N, 3·3%).

Pimelanilodimethylamide-p-arsonic Acid (II; $n = 5$; $R_2, R_3 = Me, Me$).—The methyl ester * (I) (6 g.) and 60% aqueous dimethylamine (15 c.c.) were heated under seal at 75° for 24 hours and then left at room temperature for 30 days. The dimethylamine was removed by evaporation and the crude dimethylamide, obtained on acidification, was converted into its sodium salt, p_H 7·5—8·0, with 2*N*-caustic soda. Ethyl alcohol was added till milky, and the filtrate evaporated to dryness. The *sodium* salt (4 g.) thus obtained was somewhat deliquescent (Found : hydrolysable N, 3·05. $C_{15}H_{22}O_5N_2AsNa,3H_2O$ requires hydrolysable N, 3·0%). *Pimelanilodimethylamide-p-arsonic acid*, from this sodium salt, crystallised from water in plates, sparingly soluble in hot alcohol (Found : hydrolysable N, 3·5. $C_{15}H_{23}O_5N_2As$ requires hydrolysable N, 3·6%).

Pimelaniloethylamide-p-arsonic Acid (II; $n = 5$; $R_2, R_3 = H, Et$).—A solution of the ethyl ester † (I) (8 g.) in 33% aqueous ethylamine (16 c.c.), left for 3 days at room temperature and worked up as described for the dimethylamide, gave a *sodium* salt (3 g.), p_H 7·5 (Found : hydrolysable N, 3·15. $C_{15}H_{22}O_5N_2AsNa,2H_2O$ requires hydrolysable N, 3·2%). *Pimelaniloethylamide-p-arsonic acid*, from this salt, crystallised from water in hexagonal prisms, moderately

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* Similar treatment of the ethyl ester (I) gave no trace of the dimethylamide.
† By analogy, the methyl ester should react more readily.

soluble in hot alcohol (Found : hydrolysable N, 3·5. $C_{16}H_{23}O_6N_2As$ requires hydrolysable N, 3·6%).

Pimelanilo-n-*propylamide*-p-*arsonic Acid* (II; $n = 5$; R_2, $R_3 = H$, Pr^a).—The methyl ester (I) (6 g.) and 60% aqueous n-propylamine were heated for 8 hours at 80° in a sealed tube. The crude propylamide, obtained in the usual way, was converted into sodium salt, p_H 8, with N-caustic soda, and ethyl alcohol added till just milky. The mixture was then warmed, and the filtrate cooled to 0°. The sodium salt crystallised, but at this stage gave low analytical figures for nitrogen. With acid, however, it gave pure *pimelanilo*-n-*propylamide*-p-*arsonic acid*, which, recrystallised from water, formed glistening leaflets (2 g.), fairly soluble in hot alcohol (Found : hydrolysable N, 3·5. $C_{16}H_{25}O_5N_2As$ requires hydrolysable N, 3·5%).

The *sodium* salt, p_H 8·0, from the free acid, crystallised from dilute alcohol in leaflets (Found : hydrolysable N, 3·1. $C_{16}H_{24}O_5N_2AsNa,H_2O$ requires hydrolysable N, 3·2%).

Pimelanilido-pp′-*diarsonic acid* was prepared by shaking pimelyl dichloride (1 g.) with a solution of atoxyl (3 g.) in water (6 c.c.) and sufficient 2N-caustic soda to maintain alkalinity, and acidifying the product. The *diarsonic acid*, after purification through its sodium salt (p_H 8), was an amorphous solid, almost insoluble in hot water and alcohol (yield, 1·5 g. from 6 g. of atoxyl) (Found : As, 26·6. $C_{19}H_{24}O_8N_2As_2$ requires As, 26·9%). The *disodium* salt, p_H 8, was precipitated from aqueous solution by addition of alcohol (Found : As, 24·8. $C_{19}H_{22}O_8N_2As_2Na_2$ requires As, 24·9%).

Suberyl Derivatives.

Methyl Hydrogen Suberate and its Acid Chloride.—Suberic acid (69·2 g.), methyl alcohol (24 c.c.), and sulphuric acid (3·5 c.c.), heated at 100° for 12 hours and worked up as described for methyl hydrogen adipate (Part IV; J., 1933, 91), gave recovered suberic acid (8 g.), methyl suberate (27 g.), and methyl hydrogen suberate (33 g.), b. p. 185—189°/17 mm., m. p. 17—19°. With thionyl chloride (1·3 mols.) the last gave a theoretical yield of its *acid chloride*, b. p. 163—165°/34 mm. (Found : Cl, 16·5. $C_9H_{15}O_3Cl$ requires Cl, 17·2%).

Ethyl hydrogen suberate and its acid chloride were prepared by the same methods.

Methyl p-*arsonosuberanilate* (I; $n = 6$, $R_1 = Me$), prepared as described for methyl p-arsonopimelanilate (p. 291), was found to be contaminated with p-arsanilic acid and suberic acid. These were removed by washing with hydrochloric acid, followed by Soxhlet extraction with hot benzene. The *methyl* ester then crystallised from water in curved leaflets, soluble in hot alcohol (yield, 9 g. from 32 g. of atoxyl) (Found : As, 19·3. $C_{15}H_{22}O_6NAs$ requires As, 19·35%). The *sodium* salt crystallised from water in large plates, p_H 6·5 (Found : As, 17·2. $C_{15}H_{21}O_6NAsNa,H_2O$ requires As, 17·5%).

Ethyl p-*arsonosuberanilate* (I; $n = 6$, $R_1 = Et$), prepared from the acid chloride of ethyl hydrogen suberate and purified as described above for the corresponding methyl ester, crystallised from water in irregular leaflets, soluble in alcohol (Found : As, 19·3. $C_{16}H_{24}O_6NAs$ requires As, 18·7%). The *monosodium* salt, p_H 6·5, crystallised from water in large plates, p_H 6·5, almost insoluble in cold water (Found : As, 17·6. $C_{16}H_{23}O_6NAsNa$ requires As, 17·7%). The *disodium* salt, p_H 8·5, was very soluble in cold water (Found : As, 17·4. $C_{16}H_{22}O_6NAsNa_2$ requires As, 16·8%).

p-*Arsonosuberanilic acid* (I; $n = 6$, $R_1 = H$), readily obtained by hydrolysis of the above esters, crystallised from water in hexagonal needles, insoluble in alcohol (Found : As, 19·8. $C_{14}H_{20}O_6NAs$ requires As, 20·0%). The *sodium* salt, p_H 6·5, was very soluble in water (Found : As, 17·9. $C_{14}H_{19}O_6NAsNa,H_2O$ requires As, 18·1%).

p-*Dichloroarsinosuberanilic acid*, from the above acid (I; $R_1 = H$) by reduction, crystallised from toluene in ill-defined nodules, m. p. 152—156°, which, like p-dichloroarsinopimelanilic acid (p. 291), gave low analytical figures for chlorine (Found : Cl, 17·0. $C_{14}H_{18}O_2NCl_2As$ requires Cl, 18·0%).

Hydrolysis gave p-*oxyarsinosuberanilic acid*, separating from water, in which it is sparingly soluble, as an amorphous solid (Found : As, 21·75. $C_{14}H_{18}O_4NAs$ requires As, 22·1%).

Suberanilamide-p-*arsonic Acid* (II; $n = 6$; R_2, $R_3 = H$, H).—The methyl ester (I) (6 g.) and concentrated aqueous ammonia (18 c.c.) were heated at 100° for 12 hours. The crude amide, obtained by acidification, was converted into its *sodium* salt (p_H 6·5), which crystallised from water in leaflets, p_H 6·5 (0·75 g.) (Found : hydrolysable N, 3·2. $C_{14}H_{20}O_5N_2AsNa,2H_2O$ requires hydrolysable N, 3·3%). *Suberanilamide*-p-*arsonic acid*, from its sodium salt, crystallised from water in needles, insoluble in alcohol (Found : hydrolysable N, 3·6. $C_{14}H_{21}O_5N_2As$ requires hydrolysable N, 3·8%).

Suberanilomethylamide-p-*arsonic Acid* (II; *n* = 6; R₂, R₃ = H, Me).—The methyl
(I) (4 g.) and 33% aqueous methylamine (10 c.c.) were kept at 100° for 4 hours, and the crude
acid obtained from this mixture converted into *sodium* salt, p_H 6·5, crystallising from water in
leaflets (1 g.) (Found : hydrolysable N, 3·4. $C_{15}H_{22}O_5N_2AsNa$ requires hydrolysable N, 3·4%).
Suberanilomethylamide-p-*arsonic acid*, from its sodium salt, crystallised from water in rosettes of
needles, insoluble in alcohol (Found : hydrolysable N, 3·6. $C_{15}H_{22}O_5N_2As$ requires hydrolysable
N, 3·6%).

Suberanilodimethylamide-p-*arsonic Acid* (II; *n* = 6; R₂, R₃ = Me, Me).—The methyl ester
(I) (10 g.) and 65% aqueous dimethylamine (30 c.c.) were heated at 100° for 12 hours with
occasional shaking. The upper layer of dimethylamine was removed, and the lower layer
acidified. The crude dimethylamide, thus obtained, was converted into its *sodium* salt (p_H 6·0),
which crystallised from water in well-defined prisms (3 g.) (Found : hydrolysable N, 3·2.
$C_{16}H_{24}O_5N_2AsNa,H_2O$ requires hydrolysable N, 3·2%). *Suberanilodimethylamide*-p-*arsonic
acid*, from this sodium salt, was indefinitely crystalline and fairly soluble in hot alcohol (Found :
hydrolysable N, 3·25. $C_{16}H_{25}O_5N_2As$ requires hydrolysable N, 3·5%).

Suberaniloethylamide-p-*arsonic Acid* (II; *n* = 6; R₂, R₃ = H, Et).—The *sodium* salt of this
acid, prepared from the methyl ester (I) and 65% aqueous ethylamine as described above for the
corresponding dimethylamide, crystallised from water in rectangular plates (yield : 0·6 g. from
4 g. of methyl ester) (Found : hydrolysable N, 3·2. $C_{16}H_{24}O_5N_2AsNa,H_2O$ requires hydrolysable
N, 3·2%).

The *ethylamide* from this salt crystallised from water in minute leaflets, fairly soluble in hot
alcohol (Found : hydrolysable N, 3·3. $C_{16}H_{25}O_5N_2As$ requires hydrolysable N, 3·5%).

Suberanilide-pp'-*diarsonic Acid*.—Suberyl dichloride (10 g.) and 6N-caustic soda (35 c.c.)
were shaken in small portions with atoxyl (30 g.) in water (100 c.c.) at 50°. The solid obtained
by acidification was twice washed with boiling water and further purified through its sodium
salt. The *diarsonic acid* was a white amorphous solid, insoluble in water and alcohol (Found :
As, 25·8. $C_{20}H_{26}O_6N_2As_2$ requires As, 26·2%). The *disodium* salt (p_H 8) was isolated by alcoholic
precipitation (Found : As, 23·2. $C_{20}H_{24}O_6N_2As_2Na_2,2H_2O$ requires As, 23·0%).

61. *A New Synthesis of* 3 : 11-*Dimethoxyoxyprotoberberine, and Syn-
theses of* 2 : 3-*Methylenedioxy-*11 : 12-*dimethoxyoxyprotoberberine
and* 2 : 3 : 11 : 12-*Tetramethoxyoxyprotoberberine.*

By SATYENDRA N. CHAKRAVARTI and M. SWAMINATHAN.

IN order to obtain experimental evidence for the structure (I) assigned to 3 : 11-dimethoxy-
tetrahydroprotoberberine by Chakravarti, Haworth, and Perkin (J., 1927, 2267), 3 : 11-
dimethoxyoxyprotoberberine (III) has been synthesised in the following manner : 5-
*methoxyhomophthalo-*β-*m-methoxyphenylethylimide*, prepared from 5-methoxyhomophthalic
acid and β-*m*-methoxyphenylethylamine, was converted by hydrolysis into the corre-
sponding *amic acid* (II), the *methyl* ester of which, on treatment with phosphoryl chloride,
gave a 50% yield of 3 : 11-dimethoxyoxyprotoberberine, m. p. 143°, identical with that
obtained by Chakravarti, Haworth, and Perkin from 3 : 11-dimethoxytetrahydroproto-
berberine (*loc. cit.*).
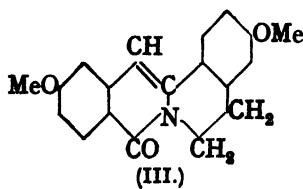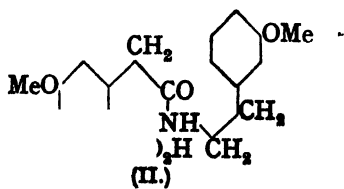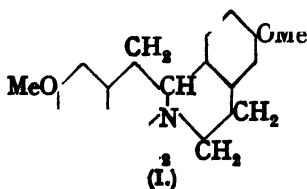
This synthesis proves that in the conversion of formyl-6-methoxy-1-(3'-methoxy-
benzyl)-1 : 2 : 3 : 4-tetrahydro*iso*quinoline into 3 : 11-dimethoxydihydroprotoberberine
the ring closure takes place in the para-position to the 3'-methoxy-group, but still leaves

the constitution of the dimethoxytetrahydroprotoberberine undetermined, since in (II) ring closure can occur in the para-position (giving III) or in the ortho-position to the methoxy-group. To decide this point a new method of synthesis is being developed, an account of which is reserved for a future communication.

In order to throw further light on the constitutions of 2 : 3-methylenedioxy-11 : 12-dimethoxytetrahydroprotoberberine and 2 : 3 : 11 : 12-tetramethoxytetrahydroprotoberberine obtained by us (*J. Indian Chem. Soc.*, 1934, **11**, 107), the corresponding oxyberberine analogues have been synthesised.

Synthesis of 11 : 12-Dimethoxy-2 : 3-methylenedioxyoxyprotoberberine.—This follows the lines of the preceding synthesis : 5 : 6-dimethoxyhomophthalic acid ——> 5 : 6-*dimethoxyhomophthalo-β-piperonylethylimide* ——> *amic acid* (as II), the *methyl* ester of which, on treatment with phosphoryl chloride, gives a substance, m. p. 231°, having the properties of an oxyberberine. This substance is represented by a formula as (III), the alternative formula (IV) being very improbable. The substance is identical with 11 : 12-
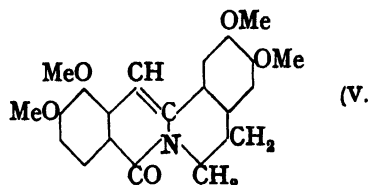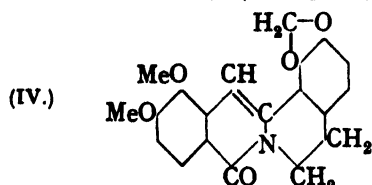
(IV.)   (V.)

dimethoxy-2 : 3-methylenedioxyoxyprotoberberine obtained from the corresponding tetrahydroprotoberberine (Chakravarti and Swaminathan, *loc. cit.*).

The method of synthesising 2 : 3 : 11 : 12-*tetramethoxyoxyprotoberberine* (V) from 5 : 6-dimethoxyhomophthalic acid and β-veratrylethylamine is similar to those outlined above. The substance is identical with 2 : 3 : 11 : 12-tetramethoxyoxyprotoberberine obtained from 2 : 3 : 11 : 12-tetramethoxytetrahydroprotoberberine.

Experimental.

5 - *Methoxyhomophthalo* - β - m - *methoxyphenylethylimide*.—A mixture of 5 - methoxyhomophthalic acid (10 g.) and β-*m*-methoxyphenylethylamine (10·5 g.) was heated at 180° for 3 hours. The *imide* crystallised from glacial acetic acid in silky needles, m. p. 133° (Found : C, 70·0; H, 5·6. $C_{18}H_{19}O_4N$ requires C, 70·2; H, 5·8%).

5-*Methoxyhomophthalo*-β-m-*methoxyphenylethylamic acid* (II).—The imide (3·5 g.) was heated with *N*-sodium hydroxide (40 c.c.) for 12 hours on the steam-bath, and the solution was cooled, saturated with carbon dioxide, filtered, and acidified with hydrochloric acid; the *amic acid* crystallised from methyl alcohol in colourless needles, m. p. 167° (Found : C, 66·7; H, 6·2. $C_{18}H_{21}O_5N$ requires C, 66·5; H, 6·1%).

The methyl ester. The amic acid (2·5 g.) was dissolved in a solution of sodium bicarbonate (0·6 g.) in water (50 c.c.), and the silver salt precipitated by silver nitrate (2 g.) was washed successively with water, alcohol, and ether, dried in a vacuum, suspended in dry ether, and refluxed with excess of methyl iodide for 8 hours. The *methyl* ester deposited by the concentrated solution crystallised from benzene–light petroleum in colourless needles, m. p. 85° (Found : C, 67·0; H, 6·7. $C_{20}H_{23}O_5N$ requires C, 67·2; H, 6·4%). A little more of the ester was obtained by extracting the silver residues with boiling methyl alcohol.

3 : 11-*Dimethoxyoxyprotoberberine*.—The methyl ester (1 g.) was boiled with phosphoryl chloride (5 c.c.) for 10 minutes, a bright red solution being obtained. The excess of chloride was distilled in a vacuum, the residue dissolved in hot water, and the filtered solution basified with sodium hydroxide. The grey precipitate obtained, after being washed with water and with methyl alcohol, crystallised from dilute acetic acid in colourless needles, which did not depress the m. p. of 3 : 11-dimethoxyoxyprotoberberine (Found : C, 74·1; H, 5·7. Calc. for $C_{19}H_{17}O_3N$: C, 74·3; H, 5·5%).

5 : 6-*Dimethoxyhomophthalo*-β-*piperonylethylimide*.—5 : 6-Dimethoxyhomophthalic acid (10 g.) and β-piperonylethylamine (9 g.) were heated at 180° for 3 hours. The solid product was triturated with alcohol and crystallised from glacial acetic acid, the *imide* separating in colourless needles, m. p. 223° (Found : C, 64·9; H, 5·2. $C_{20}H_{19}O_6N$ requires C, 65·0; H, 5·1%).

5 : 6-*Dimethoxyhomophthalo*-β-*piperonylethylamic Acid*.—This was prepared from the imide

(2·6 g.) and *N*-sodium hydroxide (20 c.c.) in the same way as the preceding amic acid. It dissolved readily in glacial acetic acid, and crystallised on dilution with an equal bulk of boiling water; m. p. 245° (Found : C, 61·7; H, 5·5. $C_{20}H_{21}O_7N$ requires C, 62·0; H, 5·4%).

The *methyl* ester, prepared from the silver salt and methyl iodide, separated from dry methyl alcohol in colourless needles, m. p. 169—170° (Found : C, 62·6; H, 6·0. $C_{21}H_{23}O_7N$ requires C, 62·8; H, 5·7%).

11 : 12-*Dimethoxy*-2 : 3-*methylenedioxyoxyprotoberberine.*—The methyl ester (1 g.) was treated with phosphoryl chloride (5 c.c.) in the manner described above. The product was crystallised from boiling glacial acetic acid containing a little water; 11 : 12-dimethoxy-2 : 3-methylene-dioxyoxyprotoberberine separated in almost colourless needles, m. p. 230—231° alone or mixed with an authentic specimen.

5 : 6-*Dimethoxyhomophthalo-β-veratrylethylimide,* obtained by heating 5 : 6-dimethoxy-homophthalic acid (10 g.) and β-veratrylethylamine (10 g.) at 180° for 3 hours, crystallised from glacial acetic acid in colourless needles, m. p. 180° (Found : C, 65·0; H, 6·1. $C_{21}H_{23}O_6N$ requires C, 65·4; H, 6·0%). The *amic acid* crystallised from methyl alcohol in needles, m. p. 165° (Found : C, 62·8; H, 6·4. $C_{21}H_{25}O_7N$ requires C, 62·5; H, 6·2%), and its *methyl* ester from benzene–light petroleum in silky needles, m. p. 123° (Found : C, 63·2, H, 6·5. $C_{22}H_{27}O_7N$ requires C, 63·3; H, 6·4%). Treatment of the ester (1 g.) with phosphoryl chloride (5 c.c.) in the manner already described furnished 2 : 3 : 11 : 12-*tetramethoxyoxyprotoberberine,* which crystallised from dilute acetic acid in colourless needles, m. p 190—191° (Found : C, 68·4; H, 5·8. $C_{21}H_{21}O_5N$ requires C, 68·6; H, 5·7%).

Conversion of 2 : 3 : 11 : 12-*Tetramethoxytetrahydroprotoberberine into* 2 . 3 . 11 : 12-*Tetra-methoxyoxyprotoberberine* —The tetramethoxytetrahydroprotoberberine (1·5 g), dissolved in the minimum quantity of boiling alcohol, was mixed with anhydrous sodium acetate (4 g.), and an alcoholic solution of iodine (2%, 150 c.c.) slowly added until the coloration was permanent. The dark brown, granular periodide was collected, washed with water, suspended in hot water, and decomposed by sulphurous acid. The *iodide* separated from water, in which it was sparingly soluble, in yellow needles, m. p. 245° (Found : C, 52·4; H, 4·8. $C_{21}H_{22}O_4NI$ requires C, 52·6; H, 4·6%). The chloride was readily obtained by digesting an aqueous suspension of the iodide with excess of silver chloride for 3 hours on the steam-bath. When the filtrate was concentrated and treated with hydrochloric acid, the chloride separated as yellow needles, m p. 225°. Hot aqueous solutions of the chloride (1·5 g.) and of potassium hydroxide (6 g. in water, 24 c.c.) were mixed and heated on the steam-bath for 3 hours. The yellow mass which separated was collected and thoroughly extracted with dilute hydrochloric acid. The residue was dissolved in hot glacial acetic acid and mixed with an equal volume of boiling water; 2 : 3 : 11 : 12-tetra-methoxyoxyprotoberberine identical with the above (mixed m. p.) then separated in colourless needles, m p. 190—191°

62. *Optical Rotatory Dispersion in the Carbohydrate Group. Part V. Tetramethyl γ-Gluconolactone.*

By R. W. HERBERT, E. L. HIRST, H. SAMUELS, and C. E. WOOD.

IN marked contrast with tetramethyl γ-mannonolactone (I), the epimeric γ-glucono-lactone (II) exhibits only small variation in specific rotation when measurements in different solvents are compared (Haworth, Hirst, and Smith, J., 1930, 2659). These two substances differ structurally only in the configurations of the second carbon atoms, and since (I) has been found to display anomalous rotatory dispersion in organic solvents (Part IV, J., 1934, 1825), it was of particular interest to investigate for comparison the optical rotatory dispersion of (II).

The rotation of (I) in organic solvents can be represented by a Drude equation with two terms of opposite sign (see Table I), the frequency constants of which are identifiable with absorbing centres due (*a*) to the carbonyl group (induced dissymmetry) and (*b*) to the C–C, C–O–, and C–H valencies present in the molecule (bands in the Schumann region). The term ($\lambda_2^2 = 0·06$) representing the induced dissymmetry was in this case positive,

⋅ *Herbert, Hirst, Samuels, and Wood:*

TABLE I.

	Tetramethyl γ-mannonolactone.					Tetramethyl γ-gluconolactone.				
	H₂O.	EtOH.	CHCl₃.	Dioxan.	C₆H₆.	H₂O.	EtOH.	CHCl₃.	Dioxan.	C₆H₆.
$[\alpha]_D$ ...	+59·8°	−0·78°	−3·48°	−14·7°	−31·7°	+59·38°	+58·91°	+46·60°	+65·87°	+72·68°
$\lambda_1{}^2$	—	0·027	0·020	0·022	0·026	0·0267	0·029	0·035	0·034	0·035
$\lambda_2{}^2$	0·049	0·058	0·064	0·063	0·061	0·075	0·075	0·075	0·075	0·08
h_1	—	−12·25	−9·84	−13·15	−19·04	+22·09	+19·47	+16·53	+22·345	+23·78
h_2 ...	+17·8	+10·89	+6·52	+7·26	+7·85	−2·56	−0·59	−1·66	−1·35	−0·82

(The values of h_1 and h_2 refer to specific rotations. Full details of the observations summarised above will be found in Part IV and in the experimental section below.)

and the possibility arose that in the methylated γ-lactones a correlation (comparable with Hudson's rule for the unmethylated γ-lactones) might exist between the configuration of

the carbon atom involved in lactone formation and the sign of the induced dissymmetry. It is clear, however, that the second as well as the fourth carbon atom influences the induced effect, and it appeared probable that by comparing the rotatory dispersion constants of (I) and (II) information would be gained concerning the relative effects of these carbon atoms on the " induced " rotation term.

The experimental results now recorded reveal an unexpected contrast between the dispersions of the two epimerides. In all the solvents investigated (Table I) the rotatory dispersion of tetramethyl γ-gluconolactone departs comparatively slightly from simplicity and the rotation values are all strongly positive. The deviations from simplicity are sufficiently great to permit of the computation of two-term Drude equations which give satisfactory agreement between the observed and calculated values. Reference to the collected results (Table I) shows that the terms of the Drude equation are opposite in sign and that the positive term is much the greater numerically. This term in all cases has a value for $\lambda_1{}^2$ not far removed from 0·035, corresponding to an absorption band situated approximately at λ 1900. This wave-length is considerably higher than that of the Schumann band normally associated with C–C, C–H, and –C–O–R linkages which are the origin of the high-frequency term appearing in the rotatory dispersion of tetramethyl γ-mannonolactone. On the other hand, the wave-length is lower than that of the low-frequency term of the latter lactone (λ_2 *ca.* 2500). It is well known, however, that one of the absorption bands of the carboxyl group is situated in this neighbourhood (λ 1900), and it seems probable that the term having $\lambda_1{}^2$ *ca.* 0·035 in the equations for tetramethyl γ-gluconolactone is to be correlated with the induced dissymmetry of the lactonic carboxyl group. Should this be the case, it follows that in tetramethyl γ-gluconolactone the induced dissymmetry originating mainly from the fourth carbon atom controls the direction of rotation in all the solvents investigated. In this case, no term with λ^2 *ca.* 0·02 is evident, and it may be concluded that the high-frequency terms contributed by the centres of dissymmetry other than the induced centre almost or entirely cancel out. In contrast with this condition, the ordinary (non-induced) term is important in tetramethyl γ-mannonolactone, with the result that in the visual region the rotation is positive in some solvents and negative in others. For the latter substance, the value of the induced frequency constant calculated from the rotational data was λ^2 0·065, corresponding with absorption at λ 2500—2600. It would appear, therefore, that the effect of the *cis*-methoxy-groups in the methylated mannonolactone is seen in the displacement, relative to its position in the case of the *trans*-modification, of the absorption wave-length by approximately 600 Å. The movement brings the absorption band of tetramethyl γ-mannonolactone into a position much nearer the characteristic band of the carboxyl group (λ 2900 approx.). This difference in the position of the

absorption band may be correlated with another important difference manifested by substances having methoxy-groups respectively *cis* and *trans* to one another on carbon atoms 2 and 3. In comparison with their epimerides, all lactones which possess *cis*-2 : 3-methoxy- (or hydroxy-) groups are extraordinarily resistant to hydrolysis.

Two points in connexion with the present observations require further discussion. The calculations lead inevitably to the conclusion that a small negative term is present in which λ_2^2 has approximately the value 0·075. The origin of this term is obscure, and within the spectral region examined its influence on the total rotation is slight. We have considered its possible association with the carbonyl group of the lactone, but the evidence at present warrants no definite assignment to any particular group, more especially as an exactly similar term has been discovered in the rotatory dispersion of tetramethyl α-methylglucoside, a substance having no carboxyl group.

The interpretation suggested above implies that the value of λ given by $\lambda_1^2 = 0·035$ has a definite physical meaning. This would not be the case if the term were fictitiously simple and in reality represented the sum of two or more terms having different values of λ. In view of the considerable spectral range covered by several of the sets of observations and the large numerical values of the observed rotations, it seems unlikely that any equation of three or more terms could be found in which λ^2 in the principal term differed appreciably from the value 0·035. It will be seen from the experimental results that in certain solvents the differences between the observed and calculated values are, although small, greater than the experimental error. It is probable, therefore, that this lactone requires at least a three-term equation to express fully its rotation, but we have been unable to devise any equation in which λ_1^2 differs seriously from the value 0·035.

2 : 3 : 5 : 6-Tetramethyl gluconic acid in water, like the corresponding mannonic acid, shows marked general absorption in the near ultra-violet. Within the spectral range available, its rotatory power can be represented by a one-term equation ($\lambda_0^2 = 0·027$). The results are recorded in the experimental section, but in view of the small numerical values of α_λ and the limited spectral range, we reserve for future discussion the interpretation of the values of λ_0^2.

EXPERIMENTAL.

Calculation of the Constants of the Drude Equation.—The following tables show that the deviation from simplicity of the rotatory dispersion of this lactone is slight, amounting to some 12% of the value of α_λ at approximately λ 3100 (see, *e.g.*, data for solutions in dioxan and chloroform). The possible experimental error, although small, is nevertheless an appreciable proportion of this divergence and renders almost impossible the direct calculation of the constants of a two-term Drude equation. Direct calculations (Lowry and Glyn Owen, *Trans. Faraday Soc.*, 1930, 26, 371) made with 4 points, distributed throughout the spectral range investigated, resulted generally in equations the solutions of which involved imaginary quantities.

The method of calculation adopted was to obtain the constant, λ_1, of an approximate one-term equation by careful extrapolation of the graph of 1/α against λ^2. A value for λ_2 was then assumed, and four experimental points, A, B, C and D, were chosen, distributed as evenly as possible throughout the spectral range examined, measurements having been taken to the limits of transparency in a 2-dm. tube. By using these values of λ_1 and λ_2, values of k_1 and k_2 were computed from the experimental points A and C, and a second pair, k_1' and k_2', from the points B and D. If λ_1 and λ_2 had been correctly chosen, it would be found that $k_1 = k_1'$ and $k_2 = k_2'$ within the experimental error, but in general this would not be the case, so λ_1 was then varied by trial and error until the differences $k_1 - k_1'$ and $k_2 - k_2'$ were as small as possible; then λ_2 was varied with the same object, and finally, by repeating the whole process of successive approximation as often as necessary, the variation of k_1 and k_2 over the whole dispersion curve was reduced to less than the experimental error or to a minimum.

This method of obtaining a two-term (4 constant) Drude equation seems to be the only one available where variations from simplicity are small. The signs of k_1 and k_2 are readily ascertainable in the preliminary stage of the calculation, but the ultimate exact evaluation of λ_1 and λ_2 and consequent values of k_1 and k_2 is a very long process.

It will be noted that the frequency constants (λ_1) of the most satisfactory simple equations which are given for comparison) are less than the corresponding constants (λ_1) of the high-frequency term in the complex equations, and that the deviation from simplicity (α, obs.—α,

calc.) is negative. It was found possible to derive more than one equation which gave reasonably close agreement between observed and calculated values. The possible variations in $\lambda_1{}^2$

Wave-length, A.U.
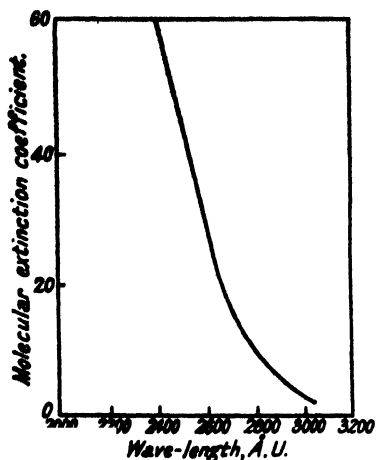
and $\lambda_2{}^2$ are, however, inconsiderable, and there is no escape from the introduction of terms containing respectively a value of $\lambda_2{}^2$ not far removed from 0·07 and of $\lambda_1{}^2$ close to 0·035. This applies even for those alternative equations (the best of several calculated) given for the dioxan and benzene solutions of the lactone, none of which is within our recognised limits of experimental error. It is highly probable, however, that the rotation of this lactone requires a more complicated function for its exact representation. Attempts were made to follow the dispersion curves into the region of absorption, but even with 2-cm. columns of solution the absorption was too great to permit accurate observations. Photometric measurements on solutions of the lactone in water, alcohol, and dioxan showed slight absorption between λ 7000 and λ 3000. Beyond λ 3000, general absorption set in, rising steeply at about λ 2700. There was no indication of selective absorption (see fig.).

Rotatory Dispersion.—Tetramethyl γ-gluconolactone was prepared by the oxidation of tetramethyl glucofuranose (see Drew, Goodyear, and Haworth, J., 1927, 1237). It was purified for the present work by several successive distillations in a vacuum; b. p. 97°/0·05 mm., m. p. 27°. The rotational measurements were made by the methods given in Part I (J., 1930, 2108).

D = Algebraical difference between observed and calculated values.

2 : 3 : 5 : 6-*Tetramethyl gluconic acid in water*: $c = 7\cdot228$; $t = 20°$; $l = 2$ dm.; $[\alpha]_\lambda^{20°} = 6\cdot917\alpha_\lambda$; $[\alpha]_D^{20°} = 22\cdot90°$; $\alpha_\lambda = 1\cdot06/(\lambda^2 - 0\cdot027)$.

λ.	α, obs.	D.	λ.	α, obs	D	λ.	α, obs.	D.	λ.	α, obs.	D.
6708	+2·57°	+0·06	5515	+3·82°	±0	4538	+5·91°	−0·01	4010	+7·91°	−0·01
6292	2·87	±0	5225	4·31	±0	4376	6·41	−0·03	3920	8·41	+0·04
5893	3·31	±0	4887	4·98	−0·02	4258	6·91	+0·04	3749	9·41	+0·05
5805	3·39	−0·03	4736	5·41	+0·04	4130	7·41	+0·03	3582	10·41	−0·05

2 : 3 : 5 : 6-*Tetramethylgluconolactone.*—*In water*: $c = 8\cdot016$; $t = 20°$; $l = 2$ dm.; $[\alpha]_\lambda^{20°} = 6\cdot238\alpha_\lambda$; $[\alpha]_D^{20°} = 59\cdot38°$; $\alpha_\lambda = 3\cdot54097/(\lambda^2 - 0\cdot0267) - 0\cdot410224/(\lambda^2 - 0\cdot075)$.

λ	α, obs	D	λ	α, obs	D	λ	α, obs	D	λ	α, obs	D
6708	+7·24°	−0·03	5225	+12·24°	−0·07	4376	+17·91°	−0·06	3720	+25·41°	+0·17
6292	8·30	−0·01	4887	14·10	−0·09	4216	19·41	−0·04	3601	26·91	+0·02
6104	8·86	±0	4844	14·41	−0·05	4072	20·91	−0·03	3498	28·41	+0·05
5893	9·52	−0·02	4694	15·41	−0·06	3952	22·41	+0·11	3352	30·41	+0·05
5805	9·81	−0·03	4568	16·41	+0·02	3822	23·91	+0·02	3200	32·41	+0·60
5515	10·96	−0·01									

In alcohol: $c = 11\cdot2112$; $t = 25°$; $l = 2$ dm.; $[\alpha]_\lambda^{25°} = 4\cdot46\alpha_\lambda$; $[\alpha]_D^{25°} = 58\cdot91°$; $\alpha_\lambda = 4\cdot365853/(\lambda^2 - 0\cdot02895) - 0\cdot131958/(\lambda^2 - 0\cdot075)$.

λ	α, obs	D	λ	α, obs	D	λ	α, obs	D	λ	α, obs	D
6708	+10·01°	−0·01	5515	+15·29°	+0·01	4354	+26·04°	±0	3581	+41·64°	+0·15
6292	11·45	−0·04	5225	17·22	±0	4099	30·04	+0·07	3453	45·44	+0·06
6104	12·23	−0·03	4886	20·04	+0·04	3898	33·84	+0·05	3318	50·04	−0·01
5805	13·62	−0·05	4682	22·04	+0·01	3786	36·24	±0	3235	52·44	−0·22

In chloroform: $c = 7\cdot586$; $t = 25°$; $l = 2$ dm.; $[\alpha]_\lambda^{25°} = 6\cdot591\alpha_\lambda$; $[\alpha]_D^{25°} = 46\cdot60$; $\alpha_\lambda = 2\cdot5082/(\lambda^2 - 0\cdot0346) - 0\cdot251375/(\lambda^2 - 0\cdot075)$ (Equation A); $\alpha_\lambda = 2\cdot262/(\lambda^2 - 0\cdot028)$ Equation B).

λ	α, obs.	Diff. (A).	Diff. (B).	λ	α, obs.	Diff. (A).	Diff. (B).	λ	α, obs.	Diff. (A).	Diff. (B).
6708	+5·40°	+0·03°	+0·04°	5225	+ 9·23°	−0·02°	±0°	3821	+19·01°	+0·03°	−0·16
6292	6·15	−0·01	±0	4887	10·73	−0·02	±0	3660	21·01	+0·03	−0·34
6104	6·54	−0·04	+0·03	4589	12·41	+0·01	+0·01	3514	23·01	−0·03	−0·68
5893	7·07	+0·03	−0·01	4360	13·91	−0·04	−0·04	3322	26·01	+0·01	−1·46
5805	7·32	−0·01	±0	4179	15·41	+0·02	−0·02	3188	28·01	+0·03	−2·71
5515	8·20	−0·01	+0·01	4000	17·01	−0·03	−0·13	3107	29·21	+0·38	−3·80

In *dioxan*: $c = 11.416$; $t = 25°$; $l = 2$ dm.; $[α]_λ^{25°} = 4.38α_λ$; $[α]_D^{25°} = 65.87°$; $α_λ = 5.10172/(λ² − 0.03415)—0.337626/(λ² − 0.075)$ (Equation A); $α_λ = 5.04994/(λ² − 0.0333)—0.282324/(λ² − 0.075)$ (Equation B); $α_λ = 4.73/(λ² − 0.032)$ (Equation C).

λ	a, obs.	Diff. (A).	Diff. (B).	Diff. (C.)	λ	a, obs.	Diff. (A).	Diff. (B).	Diff. (C).
6708	+11·35°	−0·02°	−0·02°	+0·03°	4101	+34·43°	−0·01°	+0·02°	−0·30°
6292	13·03	−0·02	−0·02	+0·03	3983	37·08	+0·11	+0·17	−0·27
6104	13·91	−0·02	−0·02	+0·02	3850	40·06	±0	−0·02	−0·64
5893	15·04	−0·01	±0	+0·04	3720	43·46	−0·15	−0·14	−1·00
5805	15·52	−0·04	−0·03	+0·01	3588	47·64	−0·02	−0·02	−1·26
5515	17·42	−0·01	+0·01	+0·04	3520	50·04	+0·10	+0·07	−1·43
5225	19·60	−0·05	−0·04	−0·03	3444	52·64	+0·02	−0·08	−1·97
4887	22·84	−0·03	−0·01	−0·03	3364	55·64	−0·08	−0·19	−2·64
4681	25·27	+0·03	+0·05	−0·01	3285	58·84	−0·06	−0·26	−3·47
4564	26·84	+0·08	+0·10	+0·01	3200	62·44	+0·01	−0·34	−4·75
4445	28·44	−0·03	±0	−0·13	3144	64·84	+0·15	−0·36	−5·92
4259	31·44	−0·04	−0·01	−0·22	3097	67·24	+0·78	+0·09	−6·77
4216	32·28	+0·04	+0·07	−0·17	3020	69·64	+1·05	−0·15	−10·25

In *benzene*: $c = 10.662$; $t = 25°$; $l = 2$ dm.; $[α]_λ^{25°} = 4.6896α_λ$; $[α]_D^{25°} = 72.83°$; $α_λ = 5.354337/(λ² − 0.0398)—0.511828/(λ² − 0.075)$ (Equation A); $α_λ = 5.07/(λ² − 0.035)—0.175/(λ² − 0.08)$ (Equation B).

λ	a, obs.	Diff. (A).	Diff. (B).	λ	a, obs.	Diff. (A).	Diff. (B).	λ	a, obs.	Diff. (A).	Diff. (B).
6708	+11·76°	+0·07°	+0·01°	4755	+25·41°	+0·06°	+0·08°	3694	+46·91°	−0·15°	+0·04°
6270	13·52	−0·02	−0·08	4603	27·41	+0·03	+0·08	3622	49·41	−0·07	+0·13
6104	14·35	−0·02	−0·07	4472	29·41	+0·07	+0·14	3551	51·91	−0·12	+0·05
5880	15·63	+0·02	−0·03	4293	32·41	+0·04	+0·13	3488	54·41	−0·03	+0·11
5805	16·08	−0·01	−0·03	4090	36·41	−0·04	+0·09	3415	57·41	+0·01	+0·07
5515	18·00	−0·02	−0·05	3957	39·41	−0·17	±0·00	3345	60·41	+0·01	−0·04
5225	20·35	−0·03	−0·04	3774	44·41	−0·17	+0·12	3259	64·41	+0·19	−0·11
4887	23·75	−0·03	−0·02	3709	46·41	−0·18	+0·03	3190	67·41	+0·13	−0·49

63. *The Constitution of Apocinchene and Syntheses of its Methyl and Ethyl Ethers.*

By J. KENNER and F. SYDNEY STATHAM.

IN the course of their investigations on the constitution of the cinchona alkaloids Comstock and Koenigs observed a remarkable reaction whereby cinchene and quinene were respectively converted by prolonged boiling with concentrated hydrobromic acid into apocinchene and apoquinene (*Ber.*, 1881, **14**, 1885; 1894, **27**, 900), but the matter has received no further attention. This is probably because Koenigs was able to show that these products represent fundamental departures in type from the alkaloids themselves. By progressive oxidation of its ethyl ether, Koenigs converted apocinchene into a 4-dicarboxyethoxyphenylquinoline, from which 4-*o*-hydroxyphenylquinoline was obtained and identified by comparison with a synthetic material, prepared by Besthorn and Jaeglé (*Ber.*, 1894, **27**, 3035). Since, further, the dicarboxylic acid yielded an anhydride, and its precursor was a quinolylethoxyacetophenonecarboxylic acid, it followed that apocinchene contained two ethyl groups and that these occupied either the 2 : 3- or the 3 : 4-position (IV) with respect to the phenolic hydroxyl group.

Of these alternatives Koenigs seemed to prefer the former, and it has been cited without qualification in the literature [compare Meyer and Jacobson, " Lehrbuch der organischen Chemie," II, (3), 1006; Brühl, " Die Pflanzenalkaloide," p. 197].

From an inspection of the formula (I) for cinchene (Koenigs, *J. pr. Chem.*, 1900, **61**, 146), however, it seemed to us highly probable that the two ethyl groups arise from the vinyl group and from the two bridge methylene groups respectively, and therefore that apocinchene should be represented by (IV). The detailed mechanism of the change remains

somewhat obscure, but in view of Lipp's work on the relationships of β-amino-ketones and the corresponding tetrahydropyridines (*Ber.*, 1905, **38**, 2474; *Annalen*, 1915, **409**, 79) it would seem that the idea of conversion of cinchene into the ketone (II) could be entertained at the most for dilute acid solutions, in which the formation of lepidine and meroquinene is observed (Koenigs, *Ber.*, 1890, **23**, 2677; 1894, **27**, 900) :
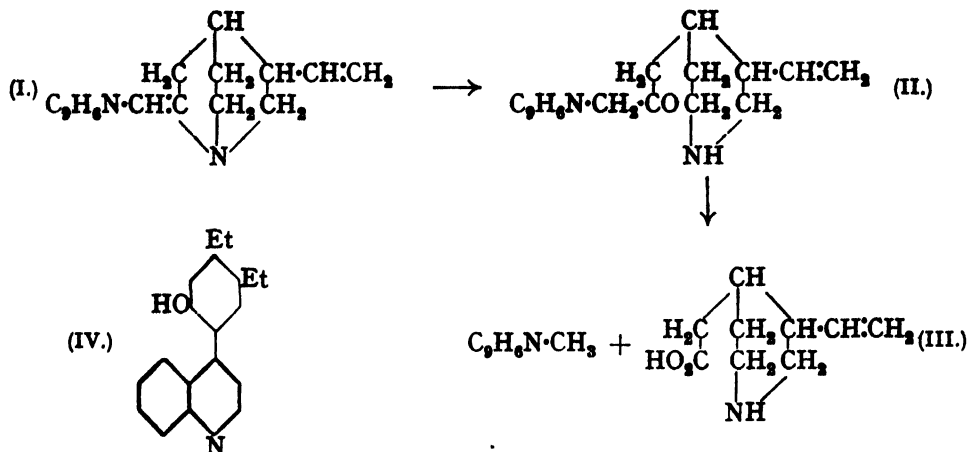
A different mechanism must be sought for strongly acid solutions, and is probably to be connected with the formation of olefins by decomposition of the salts of amines.

In order to test our views, we undertook the synthesis of (IV) and, as a preliminary, decided to examine the possibility of extending the method of Blaise and Maire (*Bull. Soc. chim.*, 1908, **3**, 658, 667) from aliphatic to aromatic β-chloroethyl ketones :
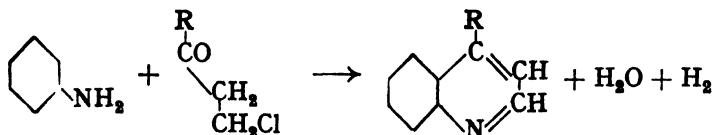
In this manner, 4-phenylquinoline was readily obtained, and although, as we had anticipated from the observations of Blaise and Maire in the aliphatic series, we only obtained a very moderate yield (10%), this was amply compensated by the directness of the method as contrasted with that employed by Besthorn and Jaeglé in their work.

Although the yields were still smaller in the cases of the phenolic ethers, it was clear that the application of the method to 3 : 4-*diethyl-anisole* and *-phenetole* was sufficiently practicable for our purpose. The identity of the solid ethyl ether, as well as of the *picrates* derived from each of the synthetic bases with the respective products prepared from authentic apocinchene, served to confirm our prediction. Although the preference of Koenigs is thus shown to have been wrong, it must in fairness be stated that he conceived the reaction as involving an olefinic intermediate product (*J. pr. Chem.*, *loc. cit.*).

m-Ethylphenol, the starting material for the preparation of 3 : 4-diethylanisole, was prepared from *m*-hydroxyacetophenone by Clemmensen's method of reduction, and also by decomposition of its semicarbazone with potassium hydroxide. It has been isolated from coal tar by Kruber and Schmitt (*Ber.*, 1931, **64**, 2270). Conversion of the phenol through its acetate successively into 4-*hydroxy-2-ethylacetophenone* and 3 : 4-*diethylphenol* was carried out along familiar lines. The constitutions of the products follow by analogy with those prepared under the same conditions from *m*-cresol (Rosenmund and Schnurr, *Annalen*, 1928, **460**, 65), and we have independently confirmed that of the ketone by converting it, with the aid of hydrogen peroxide (compare Baker, *J.*, 1934, 1678), into 2-ethylquinol. *m*-Ethylphenyl acetate exhibits a much smaller tendency than *m*-tolyl acetate to yield a *p*-hydroxyacetophenone derivative.

EXPERIMENTAL.

4-Phenylquinoline.—Hale and Britton (*J. Amer. Chem. Soc.*, 1919, **41**, 845) claim a 90% yield of β-chloropropiophenone, m. p. 57°. Conant and Kirner, however (*ibid.*, 1924, **46**, 240), record a melting point of 49—50° for the ketone, and a repetition of Hale and Britton's work has now yielded a mixture of products, m. p. 71—72° (obviously 1 : 3-diphenylpropan-1-one, for which Schneidewind, *Ber.*, 1888, **21**, 1325, gives m. p. 72—73°) and m. p. 49—50° respectively. In confirmation of Conant's work, the latter melting point could not be raised by crystallisation from light petroleum or alcohol. Hale and Britton's procedure was therefore modified by heating β-chloropropionic acid (20 g.) with phosphorus trichloride (18 g.) on the water-bath for 1 hour, treating the product with carbon disulphide (30 c.c.), and adding the filtered mixture slowly to a mixture of benzene (14 g.), carbon disulphide (30 c.c.), and aluminium chloride (24 g.). After being gently warmed for ¼ hour, the mixture was poured on ice. A crude product (30 g.), m. p. 30—40°, remaining after spontaneous evaporation of the solvent was crystallised from light petroleum. Unnecessary heating of this ketone and its derivatives described below must be avoided.

β-Phenylaminopropiophenone, obtained when the chloro-ketone (1·1 g.) and aniline (1·4 g.) were heated with water (2 g.) for ¼ hour at 100°, crystallised from alcohol in white shining plates, m. p. 111—112° (Collet, *Bull. Soc. chim.*, 1897, **17**, 80, gives m. p. 111—112°).

It was, however, unnecessary to isolate this in the preparation of 4-phenylquinoline. The pure chloro-ketone (16·8 g.) was heated for 1 hour at 100° with aniline (18·6 g.), aniline hydrochloride (12·95 g.), and ethyl alcohol (13 g.), the mixture made alkaline with potassium hydroxide, and the base extracted with ether and dried over potassium carbonate. The fraction (11 g.), b. p. 100—290°/20 mm., was heated for 1 hour at 100° with acetic anhydride (12 g.). The unacetylated base (4 g.), extracted from the mass, was treated with alcoholic picric acid solution. The picrate separated from alcohol in yellow needles, m. p. 225° (Found : C, 58·0; H, 3·6; N, 13·0. Calc. for $C_{21}H_{14}O_7N_4$: C, 58·1; H, 3·2; N, 12·9%). Koenigs and Meimberg record 224° as the m. p. of 4-phenylquinoline picrate (*Ber.*, 1895, **28**, 1039).

A similar procedure was applied to various derivatives of benzene, and the relevant details of m. p., analyses, and yields are tabulated below. The last two instances given are those which respectively furnish the methyl and the ethyl ether of apocinchene. The validity of the melting points of the picrates and their mixtures as tests of identity was specially tested. In all cases sensible depression of melting point was observed when different picrates were mixed.

Substituents.	Chloro-ketone. M. p. and analysis (theo. figures below).	M. p. of anilide.	B. p. of basic portion used for acetyl- ation.	M. p. and analysis of picrate isolated (theo. figures below).	Yield, %.
4-Methoxy	63—64° C, 60·1; H, 5·8; Cl, 18·0 (C, 60·4; H, 5·5; Cl, 17·9%)	130°	100—300°/ 20 mm.	232—234° (decomp.), shrinks and darkens at 223° C, 56·7; H, 3·7; N, 12·0 (C, 56·9; H, 3·4; N, 12·1%)	6
4-Methyl	80—81° C, 65·5; H, 6·3; Cl, 19·3 (C, 65·7; H, 6·0; Cl, 19·4%)	120	100—300/ 20 mm.	206° (decomp.), shrinks at 197° C, 58·6; H, 4·0; N, 12·8 (C, 58·9; H, 3·6; N, 12·5%)	7
2-Methoxy-5- methyl	60° C, 62·3; H, 6·3; Cl, 16·4 (C, 62·1; H, 6·1; Cl, 16·7%)		100—300/ 20 mm.	213° (decomp.) C, 57·4; H, 4·1; N, 11·4 (C, 57·7; H, 3·8; N, 11·7%)	5
4 : 5-Dimethyl	71—72° C, 67·0; H, 6·9; Cl, 18·1 (C, 67·2; H, 6·6; Cl, 18·1%)	93—94	100—290/ 20 mm.	250—253° (decomp.), darkens at 241° C, 60·0; H, 4·2; N, 12·3 (C, 59·7; H, 3·9; N, 12·1%)	9
2-Methoxy- 4 : 5-di- methyl	76—77° C, 64·3; H, 6·7; Cl, 15·7 (C, 64·0; H, 6·7; Cl, 15·8%)		110—280/ 30 mm.	215° (decomp.) C, 58·3; H, 4·3; N, 11·6 (C, 58·5; H, 4·1; N, 11·4%)	3
2-Methoxy- 4 : 5-di- ethyl	41° C, 65·7; H, 7·8; Cl, 14·1 (C, 66·0; H, 7·5; Cl, 14·0%)		100—280/ 20 mm.	200° decomp.), darkens at 197° C, 60·2; H, 4·8; N, 11·0 (C, 60·0; H, 4·6; N, 10·8%)	3
2-Ethoxy- 4 : 5-di- ethyl	81—82° C, 66·9; H, 8·1; Cl, 12·9 (C, 67·0; H, 7·8; Cl, 13·2%)		from 100/ 20 mm. to 250/ 0·5 mm.	180—181° (decomp.) N, 10·5 (N, 10·5%)	1

m-Ethylphenol.—Comparative experiments on the nitration of acetophenone (Rupe, Braun, and Zembruski, *Ber.*, 1901, **34**, 3623; Mayer and English, *Annalen*, 1918, **417**, 82) showed it to be essential to use the pure crystalline ketone, and the best results followed when a mixture of the ketone (240 g.) with sulphuric acid (d 1·98; 660 c.c.) at − 10° was treated as quickly as possible with a mixture of nitric acid (d 1·42; 140 c.c.) and sulphuric acid (d 1·98; 300 c.c.), consistent with maintenance of the temperature below 0°; after being stirred for 1 hour, the whole was poured on ice (3 kg.). By crystallising the yellowish-white solid from alcohol (500 c.c.), *m*-nitroacetophenone (240 g.), m. p. 80—81°, was obtained. Its reduction was carried out satisfactorily by West's process (J., 1925, **127**, 494), but rather better results were obtained when a solution of the nitro-ketone (30 g.) and aqueous ammonia (d 0·880; 16 c.c.) in alcohol (120 c.c.) was saturated with hydrogen sulphide, and the whole boiled for 2 hours. Yield, 24 g. *m*-Hydroxyacetophenone (Rupe and Majewski, *Ber.*, 1900, **33**, 3407) was converted into its *semicarbazone*, m. p. 194—196° (Found : N, 21·8. $C_9H_{11}O_2N_3$ requires N, 21·8%), and when an intimate mixture of this (10 g.) with potassium hydroxide (9 g.) was heated at 190° (compare Rabe and Jantzen, *Ber.*, 1921, **54**, 925), *m*-ethylphenol was obtained in quantitative yield; it was identified by conversion into its benzoate, m. p. 50° (Béhal and Choay, *Bull. Soc. chim.*, 1894, **11**, 212), and its p-*nitrobenzoate*, m. p. 68° (Found : N, 5·4. $C_{15}H_{13}O_4N$ requires N, 5·2%). The phenol was obtained more directly, but in much less satisfactory yield (34%), when a boiling mixture of amalgamated zinc (200 g.), water (150 c.c.), and the ketone (5 g.) was treated with hydrochloric acid (d 1·13; 100 c.c.) in the course of 20 minutes, and nine further portions of the ketone (5 g.) and acid (100 c.c.) were successively added in the same manner. Finally more acid (250 c.c.) was added and the whole boiled for 3 hours. We are indebted to Dr. G. Baddeley for carrying out this experiment.

4-Hydroxy-2-ethylacetophenone.—Freshly prepared aluminium chloride (60 g.) was added gradually to a solution of *m*-ethylphenyl acetate (50 g.), b. p. 222—223° (Béhal and Choay, *loc. cit.*), in dry nitrobenzene (125 g.) maintained at 0°. After 5 days, the mixture was decomposed by ice-water and treated with steam. The 2-hydroxy-4-ethylacetophenone thus removed awaits further examination. The material not volatile in steam consisted essentially of *4-hydroxy-2-ethylacetophenone*,* b. p. 150—152°/0·45 mm., m. p. 102° (Found : C, 73·0; H, 7·6. $C_{10}H_{12}O_2$ requires C, 73·2; H, 7·3%). The yield varied inexplicably, and only exceptionally amounted to 50% of the theoretical. The *semicarbazone* was formed only after several weeks, and obtained in clusters of long needles, m. p. 172° (Found : N, 19·2. $C_{11}H_{15}O_2N_3$ requires N, 19·0%). The ketone was therefore more readily characterised by its p-*nitrobenzoate*,* m. p. 80° (Found : N, 4·6. $C_{17}H_{15}O_5N$ requires N, 4·5%). A solution of the ketone (0·8 g.) in 2N-potassium hydroxide (5 c.c.) was treated with 3% hydrogen peroxide solution (8·5 c.c.) in an atmosphere of coal gas. After ½ hour crystals of unchanged hydroxyethylacetophenone (0·3 g.), m. p. 102°, had separated ; these were filtered off, and acidification of the dark-coloured mother-liquor gave a little impure material (0·1 g.), m. p. *ca.* 85°. Ether extraction of the liquors yielded ethylquinol, which was crystallised from benzene ; m. p. 113—115° (Found : C, 69·3; H, 7·2. Calc. : C, 69·6; H, 7·2%). Bayric (*Bull. Soc. chim.*, 1894, **11**, 1130) gives m. p. 112—113°, Johnson and Hodge (*J. Amer. Chem. Soc.*, 1913, **35**, 1019) m. p. 113—114°, and Clemmensen (*Ber.*, 1914, **47**, 55) m. p. 112°. The product did not depress the m. p. of an authentic specimen prepared from quinol (Nencki and Schmid, *J. pr. Chem.*, 1881, **23**, 546; Johnson and Hodge, *loc. cit.*; Clemmensen, *loc. cit.*).

3 : 4-Diethylphenol.—The ketone (20 g.) was reduced by boiling it with amalgamated zinc (100 g.), hydrochloric acid (60 c.c., d 1·17), and water (60 c.c.), hydrochloric acid (625 c.c.) being gradually added in the course of 6 hours to the boiling solution; the whole was boiled for a further 1¼ hours. By separating the oily layer from the cold mixture and extracting the aqueous layer with ether, *3 : 4-diethylphenol* (15 g.), b. p. 106°/0·5 mm., was isolated (Found : C, 80·0; H, 9·4. $C_{10}H_{14}O$ requires C, 80·0; H, 9·3%); it was characterised by the p-*nitrobenzoate*, m. p. 81—82° (Found : N, 4·8. $C_{17}H_{17}O_4N$ requires N, 4·7%). A mixture of its *acetate* (17·7 g.), b. p. 113—115°/0·35 mm. (Found : C, 74·9; H, 8·1. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%), with aluminium chloride (26·5 g.) was heated at 140° for 2 hours. The resulting *2-hydroxy-4 : 5-diethylacetophenone* * (15·9 g.), b. p. 134—137°/0·75 mm. (Found : C, 74·6; H, 8·5. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%) (compare Auwers, Bundesmann, and Wieners, *Annalen*, 1926, **447**, 163), was characterised by its *semicarbazone*,* m. p. 240° (Found : N, 16·9. $C_{13}H_{19}O_2N_3$ requires N, 16·9%). Its *methyl* ether was prepared by the gradual addition of methyl sulphate (5 g.) to a solution of the phenol (4 g.) and potassium hydroxide (1·5 g.) in

* Compounds marked with an asterisk were first prepared by Mr. E. C. S. Jones in collaboration with one of us.

aqueous potassium hydroxide solution ($2N$; 12 c.c.). The operation was completed with the aid of further quantities of methyl sulphate (7·5 g.), potassium hydroxide (2 g.), and of the $2N$-solution (10 c.c.). From an ethereal extract of the resulting mixture, aqueous sodium hydroxide solution (40%) caused precipitation of the sodium salt of the unchanged phenol, and this was removed on a fritted glass filter. The required methyl ether (2·7 g.), m. p. 35—39°, was isolated from the ethereal solution, and characterised by its *semicarbazone*, m. p. 128° (Found : N, 16·1. $C_{14}H_{21}O_2N_3$ requires N, 16·0%).

The Methyl Ether of Apocinchene.—(a) Apocinchene hydrobromide (Koenigs, *J. pr. Chem.*, *loc. cit.*), was treated in the usual manner with aqueous potassium hydroxide solution ($2N$) and methyl sulphate. The oily product (Koenigs, *Ber.*, 1885, **18**, 2380) was characterised by its *picrate*, m. p. 200° (decomp.) after darkening at 197° (Found : C, 60·3; H, 4·8; N, 11·0. $C_{26}H_{24}O_8N_4$ requires C, 60·0; H, 4·6; N, 10·8%).

(b) 3 : 4-*Diethylanisole*, from the corresponding phenol, is an oil, b. p. 124—125°/23 mm. (Found : C, 80·8; H, 10·0. $C_{11}H_{16}O$ requires C, 80·5; H, 9·8%). A cooled mixture of this ether (6·6 g.), aluminium chloride (5·2 g.), and carbon disulphide (12 c.c.) was treated gradually with a solution of β-chloropropionyl chloride (from the acid, 4·3 g., and phosphorus trichloride, 3·6 g.) in carbon disulphide (12 c.c.), and the mixture at once decomposed by ice-water. Spontaneous evaporation of the carbon disulphide layer furnished 2-*methoxy*-4 : 5-*diethyl*-β-*chloropropiophenone* (4 g.). It separated from light petroleum in colourless crystals, m. p. 41° (Found : C, 65·7; H, 7·8; Cl, 14·1. $C_{14}H_{19}O_2Cl$ requires C, 66·0; H, 7·5; Cl, 14·0%). If the reaction mixture were left for ½ hour before being worked up, an oily product was produced. The details of its conversion into apocinchene methyl ether are included in the table above. The picrate of the synthetic material softened at 197° and melted at 200°, and did not depress the melting point of material derived from apocinchene itself.

The Ethyl Ether of Apocinchene (Koenigs, *Ber.*, 1885, **18**, 2381).—(a) An authentic specimen was prepared from apocinchene by use of ethyl sulphate, and converted into its *picrate*, m. p. 179—180° (Found : C, 60·4; H, 5·2; N, 10·7. $C_{27}H_{26}O_8N_4$ requires C, 60·7; H, 4·9; N, 10·5%).

(b) 3 : 4-*Diethylphenetole*, from the phenol by treatment with diazoethane, boiled at 120—125°/20 mm. (Found : C, 80·6; H, 10·4. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%), and was converted into the chloroethyl ketone and thence into apocinchene ethyl ether in the manner described for the corresponding methyl ether above. The picrate of the synthetic material melted at 179—180°, and did not depress the melting point of the authentic ethyl ether. Further, it was converted into the free base, m. p. 70—71° after crystallisation from dilute ethyl alcohol (Found : N, 4·8. $C_{21}H_{32}ON$ requires N, 4·6%). It did not depress the melting point of the authentic ether.

THE COLLEGE OF TECHNOLOGY, MANCHESTER.

64. *The Meta-alkylation of Aromatic Hydrocarbons by the Friedel–Crafts Reaction.*

By G. BADDELEY and J. KENNER.

THE action of alkyl halides on the homologues of benzene in presence of aluminium chloride has frequently been investigated, and the results of earlier workers (reviewed by Holleman, " Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910, p. 102; compare also Shoesmith and McGechen, *J.*, 1930, 2231), though frequently conflicting, provided strong indications of the formation of meta-derivatives. For instance, Shoesmith and McGechen (*loc. cit.*) obtained from toluene a mixture composed of 65—71% of *m-tert.*-butyltoluene with 35—30% of its *p*-isomeride.

The fact that such hydrocarbons on substitution otherwise invariably yield ortho-para-derivatives indicates that the anomalous result may be due not to " direct meta-substitution in the toluene nucleus " (Shoesmith and McGechen, *loc. cit.*), but to a transformation of initially formed para-derivative. An experimental basis for this view is available in the classical work of Anschütz and his collaborators (*Ber.*, 1884, **17**, 2816; 1885, **18**, 657; *Annalen*, 1886, **235**, 177) on the changes (comprising isomerisation, dealkylation, and further alkylation) undergone by various polyalkylbenzenes in presence of aluminium chloride. Anschütz (*Annalen, loc. cit.*, p. 188) connected these changes with the formation of methyl chloride and benzene from toluene and hydrogen chloride under

similar conditions, and attributed isomerisation and higher alkylation to ordinary substitution by alkyl chloride formed by dealkylation. On such a view, and consistently with the maintenance of *op*-substitution, the conversion of *p*- into *m*-xylene (Mundici, *Gazzetta*, 1904, **84**, 221; Heise and Töhl, *Annalen*, 1892, **270**, 155) is perhaps most plausibly expressed as follows:

$$1 : 4\text{-}C_6H_4Me_2 \xrightarrow{\text{MeCl}} 1 : 3 : 4\text{-}C_6H_3Me_3 + HCl \longrightarrow 1 : 3\text{-}C_6H_4Me_2 + MeCl$$

Some time ago (compare *J. Soc. Chem. Ind.*, 1933, **52**, 469) one of us pointed out that such a hypothesis would also involve isomerisation of the alkyl group in suitable cases, and indicated an intention to apply this criterion. As a preliminary, we showed that *p-n*-propylphenol is converted by oxidation into *n*-propylquinol (J., 1934, 633), and we have now studied the behaviour of *m*- and *p*-di-*n*-propylbenzene, as well as of 1 : 2 : 4-*tri*-*n-propylbenzene*, towards aluminium chloride. Heise and Töhl (*loc. cit.*, p. 164) have already stated that the change of *n*-propylbenzene into *m*- and *p*-dipropylbenzene does not involve any modification of the propyl group, but the *m*-isomeride itself was only obtained by Heise (*Ber.*, 1891, **24**, 768) as one of the products of this reaction. In view of the importance of the matter, we have prepared the various hydrocarbons required for our purpose by methods which leave no doubt as to their constitution, and in doing so have to some extent amplified the work of Brady and Cunningham (J., 1933, 121) on the nitration of *n*-propylbenzene. The following scheme sufficiently indicates our procedure, orientations being established by reference to the known nitroacetamidobenzoic acids :
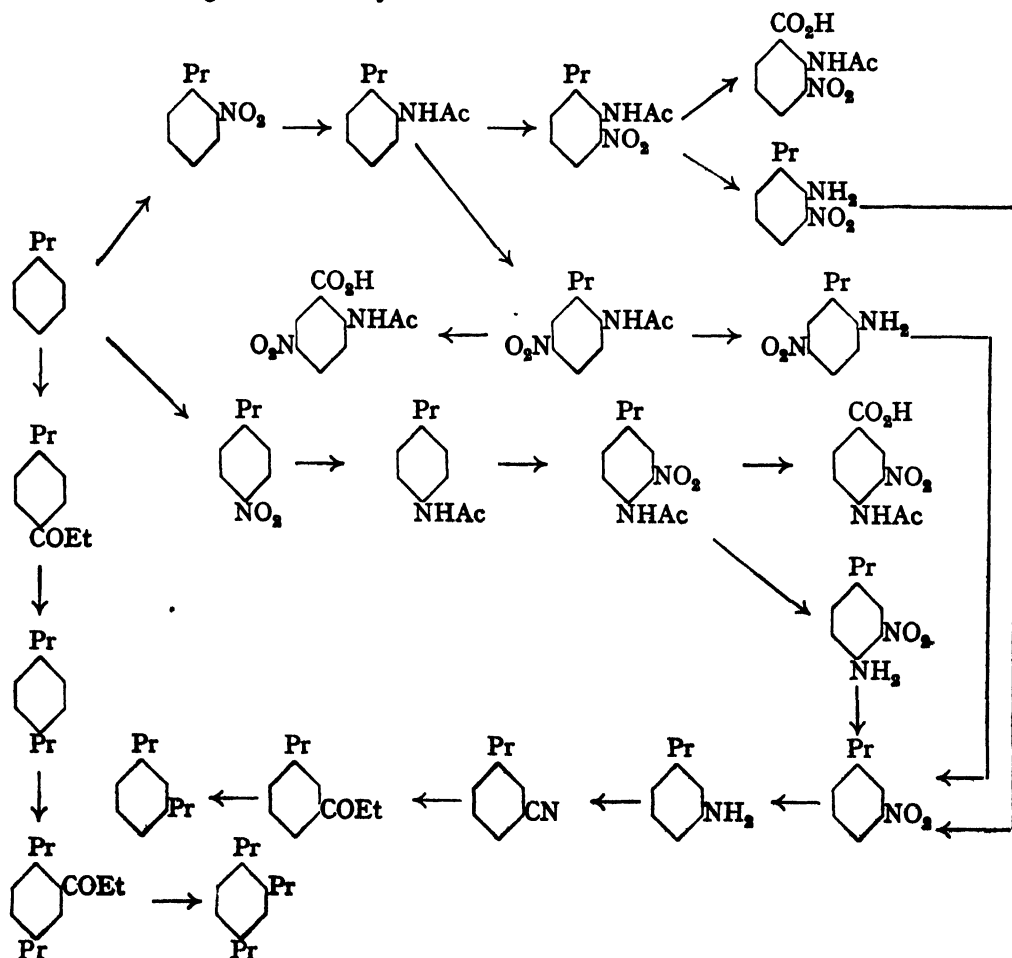
We were able to confirm the data supplied by Heise and, by using the method of separation described by him, to show that *p*-di-*n*-propylbenzene is converted to the extent of about two-thirds into the *m*-di-*n*-propylbenzene by the action of aluminium chloride for two hours at 100°. At the same time some *n*-propylbenzene and 1 : 3 : 5-tripropylbenzene were formed. Orientation of the latter was demonstrated by oxidation to trimesic acid, and there can be little doubt that the normal character of the propyl groups was preserved. Strict reversibility of the relationship between the *p*- and the *m*-isomerides cannot be expected in view of the processes of dealkylation and alkylation which also occur, and experiment showed that very little *p*-derivative was formed when *m*-dipropylbenzene was treated with aluminium chloride. 1 : 2 : 4-Tripropylbenzene was largely converted into the 1 : 3 : 5-derivative, together with lower and higher alkylated products.

Whilst it can fairly be claimed that these results definitely contradict any substitution hypothesis of the kind adumbrated above, a final decision as to the real character of the changes involved is not simple. As a preliminary it is necessary to consider the general character of the changes promoted by aluminium chloride (compare Kränzlein, " Aluminium Chlorid in der organischen Chemie," Berlin, 1932). It would seem that these arise from the strong kationoid properties of the chloride, which are themselves due to the deficiency of two electrons requisite to complete the octet of the aluminium atom. As a consequence, it is able to enter into combination or association with anionoid centres (compare, *e.g.*, Walker and Spencer, J., 1904, **85**, 1106), as protons do, and so to provide a stimulus to further reaction. Thus the hydrolysis of ethers by aluminium chloride and by hydrogen iodide respectively probably depends on formation of the complexes

$$\left[\begin{matrix}R\\R\end{matrix}\!\!>\!\!O{\cdot}AlCl_2\right]^{\boldsymbol{\cdot}} Cl' \qquad \text{and} \qquad \left[\begin{matrix}R\\R\end{matrix}\!\!>\!\!O{\cdot}H\right]^{\boldsymbol{\cdot}} I'$$

Similarly both proton and aluminium chloride stimulate the reactivity of carbonyl compounds. Thus the action of sulphuric acid in inducing condensation of carboxylic acids or other carbonyl compounds with aromatic hydrocarbons corresponds to the Friedel–Crafts reaction with acid chlorides, and it is significant that the efficiency of aluminium chloride in this connection can be reduced by the presence of such competitive anionoid centres as those of nitrobenzene and acetone (Nenitzescu and Cantuniari, *Ber.*, 1932, **65**, 807; *Annalen*, 1934, **510**, 269). The parallelism between the reactions of anionoid aromatic compounds (and therefore not of nitrobenzene) in presence of aluminium chloride and those of the Grignard reagent is particularly clear in the following reaction, which occurs simultaneously with the more usual type leading to ketone formation (Scholl and others, *Ber.*, 1932, **65**, 902; *Annalen*, 1932, **493**, 56; **494**, 201; 1934, **572**, 130, 112, 124) :
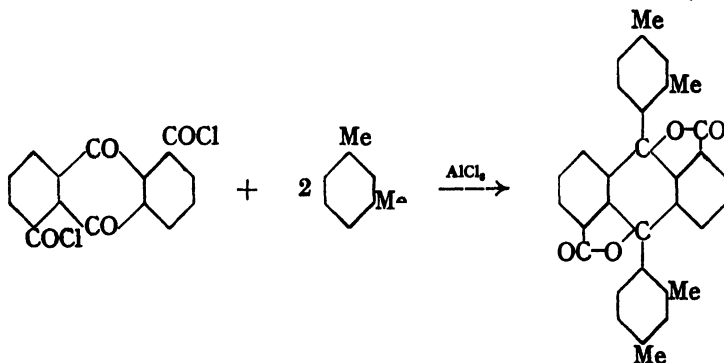
It would thus seem to be unnecessary to follow Scholl in attributing the lactone formation to tautomerism of the acid chlorides. Again, by attributing the conversion of alkyl halides into olefins to formation of the complex (I), the reaction is brought into line with the similar behaviour of the corresponding ammonium and oxonium salts :

$$R{\cdot}CH_2{\cdot}CH_2Cl \longrightarrow R{\cdot}CH_2{\cdot}CH_2Cl{,}AlCl_3 \longrightarrow R{\cdot}CH{:}CH_2 + HCl + AlCl_3$$
(I.)
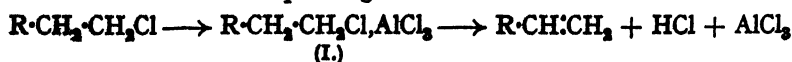
in presence of anionoid aromatic nuclei, an alternative method of relief of (I) occurs in. alkylation of the nucleus. Whilst this is stated to involve no modification of the alkyl group at low temperatures (Gustavson, *Ber.*, 1878, **11**, 1257; Kekulé and Schötter, *ibid.*, 1879, **12**, 2279; Konovalov, *Bull. Soc. chim.*, 1896, **16**, 864; Heise, *loc. cit.*), the reaction at higher temperatures can be regarded as a particular form of the Wagner–Meerwein change, in which the aromatic nucleus figures as anion compensating the β-carbon atom for migration of a hydrogen atom with one electron :

R·CH₂·CH₂Cl,AlCl₃   R·CHMe

+ H· + AlCl₄′
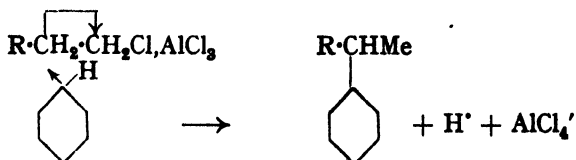
The increase in electrical conductivity observed when benzene is added to the system ethyl bromide–aluminium chloride (Wohl and Wertyporoch, *Ber.*, 1931, **64**, 1357) is in accord with this. The polymerisation of olefins is also initiated or, perhaps rather, accelerated alternatively by proton and by aluminium chloride, and would seem to depend on a " snowball " mechanism set up by these reagents :

$$\text{Me}_2\text{C:CH}_2 \longrightarrow \text{Me}_2\overset{+}{\text{C}}\text{·CH}_2\text{·AlCl}_3 \longrightarrow \text{Me}_2\overset{+}{\text{C}}\text{·CH}_2\text{·CMe}_2\text{·CH·AlCl}_3$$
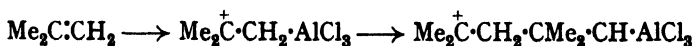
and so on.

The polymerising action of boron trifluoride on olefins (D.R.-P. 264,925; Stanley, *J. Soc. Chem. Ind.*, 1931, **49**, 349T) might have been anticipated from the close relationship between the fluoride and aluminium chloride in the sense of the Periodic System. We have found, however, that boron trichloride does not promote the Friedel–Crafts reaction.

In the light of this review, it seems clear that aluminium chloride promotes reactions in virtue of its tendency to co-ordination at anionoid centres. As a result the existing dipole condition of the molecule concerned and its reactivity are enhanced. This, however, also summarises the conditions which appear from the exhaustive work of Meerwein to be responsible for the equilibrium between camphene hydrochloride and bornyl and *iso*bornyl chlorides (*Ber.*, 1920, **53**, 1815; 1922, **55**, 2500).

The following scheme represents the application of this conception to the isomerisation we have studied, the migrant being a complex of aluminium chloride with propyl :
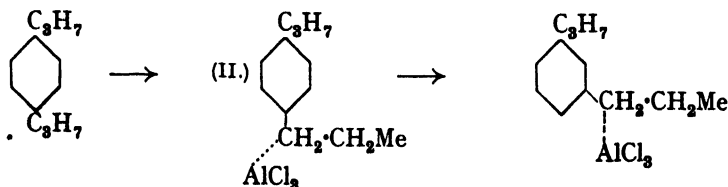
In the *m*-derivative, however, the main anionoid centre is in the para-position to one of the alkyl groups, and it is therefore at this point that the aluminium chloride ultimately attaches itself. In this way the comparative stability of *m*-dipropylbenzene is explained. The other facts which must be accommodated by any explanation of the changes in question are, on the one hand, the conversion of naphthalene derivatives into dinaphthyls as studied extensively by Scholl (compare Kränzlein, *op. cit.*, p. 73) and including that of naphthalene itself into ββ-dinaphthyl (Homer, *J.*, 1907, **91**, 1108; compare also the direct formation of β-ethylnaphthalene from naphthalene by the Friedel–Crafts reaction, Marchetti, *Gazzetta*, 1881, **11**, 265, 439; Roux, *Ann. Chim.*, 1887, **12**, 307) and, on the other, the dealkylation and the further alkylation, which accompany the simple isomerisation. The former

could readily be explained by a direct application of the foregoing suggestion as an ordinary case of substitution, followed by isomerisation :

$$\text{(diagram: H----AlCl}_3 \text{ structure)} + \text{(structure)} \longrightarrow H_2 + AlCl_3 + \text{(structure)}$$
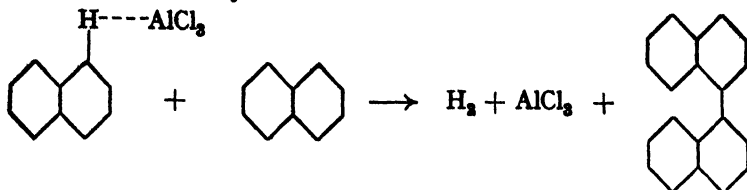
Such a formulation, however, can hardly be extended to the transference of alkyl groups from one aromatic nucleus to the other, and this is most simply attributed to radical formation, of which, indeed, in other directions such dismutation has been employed as a criterion. Nevertheless, it must not be assumed that this in any way invalidates our general thesis as to the essential character of these reactions. Radical formation is one of the results which might ensue from the condition represented by (II), and the stability of *pp'p''*-trinitrotriphenylmethyl (Ziegler and Boye, *Annalen*, 1927, **458**, 248) illustrates the way in which electron-avidity may contribute to radical formation. For the present, therefore, it seems best to regard the various experimentally observed results as consequences of varying degrees of the same general dipolar condition induced by aluminium chloride.

In conclusion, there can be little doubt that the results obtained in the cases of the di- and tri-propylbenzenes will be reproducible in other cases, so that from the purely preparative point of view a convenient means is revealed of obtaining hydrocarbons otherwise only accessible by a laborious process such as that described for *m*-di-*n*-propyl-benzene.

<div align="center">EXPERIMENTAL.</div>

The yield of propiophenone, b. p. 123°/25 mm., was increased from 50 to 88·5% by addition, until no further evolution of hydrogen chloride occurred, of further aluminium chloride (*ca.* 30 g.) to the product obtained when a mixture of propionyl chloride (150 g.) and benzene (180 g.) had been added with vigorous stirring to a suspension of aluminium chloride (150 g.) in carbon disulphide (200 c.c.). Reduction of the ketone by Clemmensen's method furnished *n*-propyl-benzene, b. p. 160° (yield, 80%). This hydrocarbon (204 g.), submitted to conditions analogous to those applied to benzene, yielded, besides unchanged material (20 g.), *p*-*n*-propylpropiophenone (196 g.), b. p. 145°/18 mm. (*semicarbazone*, needles from light petroleum, m. p. 140°. Found : C, 66·7; H, 8·3; N, 18·1. $C_{13}H_{19}ON_3$ requires C, 66·9; H, 8·2; N, 18·0%), and a fraction (20 g.), b. p. 220°/20 mm. *p*-Di-*n*-propylbenzene, b. p. 110°/20 mm., obtained from *p*-propyl-propiophenone in 50% yield by Clemmensen's method, was characterised by its sulphonamide, m. p. 105° (Heise, *Ber.*, 1891, **24**, 709, gives 106°), and converted into 2 : 5-*dipropylpropiophenone*, b. p. 160°/15 mm. (Found : C, 82·0; H, 9·7. $C_{15}H_{22}O$ requires C, 82·5; H, 10·1%). Yield, 60%. 1 : 2 : 4-*Tripropylbenzene*, b. p. 135°/20 mm., was obtained from the ketone in 60% yield (Found : C, 87·9; H, 11·6. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%).

Nitration of n-*Propylbenzene.*—This has been studied by Brady and Cunningham (*loc. cit.*), who experienced the tendency to formation of the 2 : 4-dinitro-derivative and prepared from this the *o*-nitro-derivative, b. p. 133—136°/26 mm. In our experiments, *n*-propylbenzene (75 g.) was added gradually to an ice-cooled mixture of sulphuric acid (200 c.c., *d* 1·8), nitric acid (112 c.c., *d* 1·4), and water (50 c.c.), the temperature being maintained below 15°. After ½ hour, the upper layer furnished fractions (1) 78 g., b. p. 133—140°/20 mm., (2) 8 g., b. p. 140—150°/20 mm., (3) 33 g., b. p. 150—160°/20 mm., (4) 40 g., b. p. 150°/1 mm.

On redistillation, (1) furnished practically pure *o*-nitropropylbenzene, b. p. 133°/20 mm. (Found : N, 8·6%), from which *o*-propylaniline, b. p. 112°/20 mm., was prepared by means of tin and hydrochloric acid. *o*-*Propylacetanilide* crystallised from light petroleum in needles, m. p. 93° (Found : C, 75·0; H, 8·9; N, 8·0. $C_{11}H_{15}ON$ requires C, 74·6; H, 8·5; N, 7·9%) (Piccinini and Cannozzi, *Gazzetta*, 1898, **28**, 95, assign m. p. 104—105° to the acetyl derivative of the base they prepared from 2-methyldihydroindole by reduction with hydriodic acid and phosphorus). Evidence of orientation was obtained when the anilide (17·5 g.) was gradually added to a mixture of nitric acid (50 g., *d* 1·5) and glacial acetic acid (18 g.) at 10°, and the solution left for 12 hours at the ordinary temperature. The solid, isolated by means of water,

was hydrolysed in 2 hours by boiling hydrochloric acid (40 c.c., d 1·17), and the mixture distilled in steam. The weak base thus removed was 2-*nitro-6-propylaniline*, yellow needles, m. p. 66° (Found : C, 60·1; H, 6·9; N, 15·6. $C_9H_{12}O_2N_2$ requires C, 60·0; H, 6·7; N, 15·6%), and furnished an *acetyl* derivative, needles, m. p. 140° (Found : C, 59·7; H, 6·5; N, 12·7. $C_{11}H_{14}O_3N_2$ requires C, 59·5; H, 6·3; N, 12·6%). The last was converted by oxidation at 80° with aqueous potassium permanganate in presence of magnesium sulphate into 3-nitro-2-acetamidobenzoic acid, m. p. 180°, from which the ethyl ester, m. p. 102°, was prepared by use of diazoethane. The acid and its ester did not depress the melting points of authentic specimens derived from 3-nitro-o-toluidine. 4-*Nitro-2-propylaniline* was isolated from the solution remaining after removal of the isomeride just described, and obtained in pale yellow needles, m. p. 97° (Found : C, 60·0; H, 6·9; N, 15·7%), from which an *acetyl* derivative, needles, m. p. 159°, was prepared (Found : C, 59·8; H, 6·5; N, 12·6%). This yielded 5-nitro-2-acetamidobenzoic acid, m. p. 216°, and its ethyl ester, m. p. 153°, which were each formally identified by comparison with authentic specimens.

Fraction (3), b. p. 154°/20 mm. on redistillation, was p-*nitropropylbenzene* (Found : N, 8·6. $C_9H_{11}O_2N$ requires N, 8·5%). p-Propylaniline boiled at 112°/20 mm. and furnished an *acetyl* derivative, needles, m. p. 96° (Found : C, 74·3; H, 8·7; N, 8·0. $C_{11}H_{15}ON$ requires C, 74·6; H, 8·5; N, 7·9%). By adding it (38 g.) rapidly at 30—40° to a cooled and stirred mixture of nitric acid (118 c.c., d 1·4) and sulphuric acid (47 c.c., d 1·8) and leaving the mixture for ¼ hour 2-*nitro-4-propylacetanilide*, yellow needles, m. p. 77°, was obtained (Found : C, 59·2; H, 6·7; N, 12·7. $C_{11}H_{14}O_3N_2$ requires C, 59·5; H, 6·3; N, 12·6%), from which 3-nitro-4-acetamidobenzoic acid, m. p. and mixed m. p. 221°, and its ethyl ester, m. p. and mixed m. p. 95°, were prepared. 2-*Nitro-4-propylaniline*, obtained from the acetyl derivative by hydrolysis with 50% sulphuric acid, separated from light petroleum in orange prisms, m. p. 36° (Found : C, 60·3; H, 6·9; N, 15·7. $C_9H_{12}O_2N_2$ requires C, 60·0; H, 6·7; N, 15·6%).

Fraction (4) was shown to be 2 : 4-dinitropropylbenzene (Found : N, 13·3%) by reduction to 2-nitro-4-aminopropylbenzene, m. p. 59° in accordance with the datum of Brady and Cunningham (*loc. cit.*).

m-Nitropropylbenzene (Brady and Cunningham, *loc. cit.*) was conveniently prepared by converting a mixture of o- and p-nitropropylbenzene, as obtained by the above process of nitration, into a mixture of the three nitropropylacetanilides described above. Hydrolysis of this (223 g.) with sulphuric acid (450 c.c., d 1·8) and water (810 c.c.) yielded a solution, which was diazotised (sodium nitrite, 76 g.; water, 112 c.c.), added gradually to boiling alcohol (5600 c.c.), and heated on the steam-bath for ½ hour; m-nitropropylbenzene (110 g.), b. p. 150°/20 mm., was isolated. The following constants were determined at 17° : d 1·0898; n_D 1·5334; α_D 31° 43′; γ (drop weight) 39·66; γ (drop number) 39·40. m-*Propylaniline*, b. p. 112°/20 mm., 230°/760 mm. (Found : N, 10·5. $C_9H_{13}N$ requires N, 10·4%), was characterised by an *acetyl* derivative, m. p. 53° (Found : C, 74·9; H, 8·7; N, 8·1. $C_{11}H_{15}ON$ requires C, 74·6; H, 8·5; N, 7·9%), and was converted by the Sandmeyer process into m-*propylbenzonitrile*, b. p. 127°/20 mm., which was lighter than water (Found : N, 9·8. $C_{10}H_{11}N$ requires N, 9·65%).

m-*Propylpropiophenone* was prepared by adding the nitrile (36 g.) to a solution prepared from ethyl bromide (54 g.), magnesium (12 g.), and ether (140 c.c.), and finally boiling the mixture for ½ hour. The ketone (36 g.), b. p. 145°/20 mm. (Found : C, 81·3; H, 8·8. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%), furnished a *semicarbazone*, plates, m. p. 128° (Found : N, 8·2. $C_{13}H_{19}ON_3$ requires N, 18·0%), and was converted by Clemmensen's method into m-dipropylbenzene, b. p. 105°/20 mm. (yield, 80%). This was identified by its disulphonamide, m. p. 195° (Heise, *loc. cit.*, gives 195°).

Action of Aluminium Chloride on Hydrocarbons.—(a) p-*Dipropylbenzene*. A mixture of the hydrocarbon (62 g.) and aluminium chloride (21 g.), heated on the steam-bath for 22 hours, darkened considerably, but some solid aluminium chloride remained, covered by a black oil, and an upper layer of a pale brown oil. The last became colourless, but evolved little heat, on treatment with water, whereas the black oil reacted vigorously. Fractionation of the products, however, showed them to be essentially the same. On refractionation the following main products were obtained from both layers : (1) 7 G., b. p. 67°/20 mm., identified as n-propylbenzene by conversion into 2-nitro-4-aminopropylbenzene, m. p. 59°. (2) 15 G., b. p. 105°/20 mm., sulphonated by twice its volume of fuming sulphuric acid (d 1·9) without cooling, and finally at 100° for 10 minutes. On concentration of a solution of the lead salts of the resulting sulphonic acids, that of p-dipropylbenzenesulphonic acid crystallised, and was identified by conversion into the sulphonamide, m. p. 105°. From the liquor the lead salt of m-dipropylbenzenedisulphonic acid was obtained on evaporation, and converted into the disulphonamide,

m. p. 195°. The weights of the two salts indicated that the fraction consisted of 65% of *m*- and 35% of *p*-dipropylbenzene. (3) 7 G., b. p. 135°/20 mm. Oxidation with nitric acid (1 vol., d 1·4) and water (3 vols.) at 160—200° yielded an acid, m. p. 345—350°, from which ethyl trimesate, m. p. 133°, was prepared.

(b) m-*Dipropylbenzene.* A similar experiment was carried out, and the fraction, b. p. 105°/20 mm., shown to be essentially unchanged *m*-derivative, with a very small proportion of the *p*-isomeride.

(c) 1 : 2 : 4-Tripropylbenzene (25 g.) after treatment with aluminium chloride for 4 hours at 100° yielded : (1) 7·5 g., b. p. 90—120°/20 mm., essentially *m*-dipropylbenzene, with a very little *p*-derivative; (2) 3·5 g., b. p. 120—130°/20 mm.; (3) 3·5 g., b. p. 131—140°/20 mm.; (4) 3·0 g., b. p. 140—170°/20 mm.

(2) and (3) on refractionation yielded a main fraction, b. p. 133°/20 mm., from which almost pure trimesic acid, m. p. 355° (compared with 372° for the pure acid), was obtained, and characterised by its ethyl ester, m. p. 128° before recrystallisation and m. p. 133° after one recrystallisation from alcohol. (2) and (3) were therefore mainly 1 : 3 : 5-tripropylbenzene. (4) was not examined, but, by analogy with the results obtained by Anschütz, probably consisted of tetrapropylbenzene.

COLLEGE OF TECHNOLOGY, MANCHESTER.

65. α- and β-Santalols.

By A. E. BRADFIELD, A. R. PENFOLD, and J. L. SIMONSEN.

IT has been observed by one of us (Penfold, *J. Proc. Roy. Soc. New South Wales*, 1928, **52**, 60; 1932, **66**, 240) that the essential oil from the wood of *Santalum lanceolatum* contains a lævorotatory sesquiterpenic primary alcohol, $C_{15}H_{24}O$, yielding a crystalline allophanate, m. p. 114°. Since preliminary experiments showed that this alcohol gave acetylcarbinol on oxidation, it was clear that it was closely related to the α- and the β-santalol present in the wood oil from *Santalum album*. Prior to a study of this new alcohol it appeared desirable to elucidate the structure of the dicyclic alcohol, β-santalol, and to determine its relationship to the tricyclic alcohol, α-santalol, the constitution of which has been rigidly established (for references, see Simonsen, " The Terpenes," Vol. II, p. 544).

The separation of the two santalols from each other by fractional distillation is a matter of some difficulty, and Semmler, as the result of some twenty fractionations, records $\alpha_D + 1°$ and $- 42°$ for α- and β-santalol respectively. Paolini and Divizia (*Atti R. Accad. Lincei*, 1914, **23**, II, 226) after a preliminary fractionation purified the alcohols by fractional crystallisation of the strychnine salts of the hydrogen phthalates and confirmed Semmler's values. Our experience has shown that this method is of little value except for the final purification, since the strychnine salts form mixed crystals.

By repeated distillation of Mysore oil from *S. album* under diminished pressure in carbon dioxide through a still-head of special design (Bradfield, *J. Soc. Chem. Ind.*, 1935, **54**, 6T), the progress of the separation being followed by observation of rotatory power and by oxidation with percamphoric acid (Milas and McAlevy, *J. Amer. Chem. Soc.*, 1933, **55**, 352), we have obtained both α- and β-santalol in a state of purity. α-Santalol has b. p. 166—167°/14 mm., d_{25}^{25} 0·9770, n_D^{25} 1·5017, $\alpha_{5461} + 10·3°$, $\alpha_{5780} + 9·0°$, $[R_L]_D$ 66·4 (calc., 65·93). The observed exaltation agrees well with that anticipated for a substance containing a *cyclo*propane ring. Apart from the rotatory power, these values are in close accord with those recorded by Semmler and by Paolini and Divizia. We find, however, that the strychnine salt of the hydrogen phthalate has m. p. 144—145°, not 155° as stated by the latter authors. The purity of the alcohol was checked by titration with percamphoric acid, 1·02 mols. of oxygen per mol. being absorbed.*

From the higher-boiling distillate a fraction of β-santalol, b. p. 177—177·5°/17 mm.,

* Mr. B. Sanjiva Rao, Indian Institute of Science, Bangalore, informs us that he has obtained pure α-santalol having a similarly high rotatory power.

α_{5461} — 69·2°, was obtained, which was not appreciably altered by further distillation. Determination of unsaturation by percamphoric acid showed, however, only 1·86 ethylenic linkages. The oil was therefore further purified through the strychnine salt of the hydrogen phthalate and a specimen of the pure alcohol (percamphoric acid value, 1·97) having the following constants was obtained : b. p. 177—178°/17 mm., d_{15}^{25} 0·9717, n_D^{25} 1·5100, α_{5461} —87·1, $[R_L]_D$ 67·71 (calc., 67·66). It is evident that previous specimens of this alcohol must have been highly contaminated with α-santalol.

It has been assumed, without direct experimental evidence, that β-santalol (II) or (III) is similar in structure to α-santalol (I).

(I.)   (II.)   (III.)

(R = :CMe·CH₂·OH)
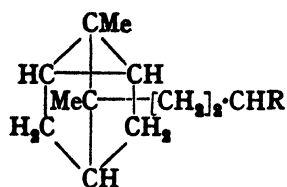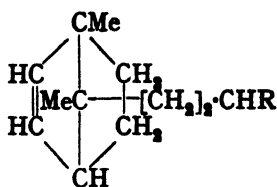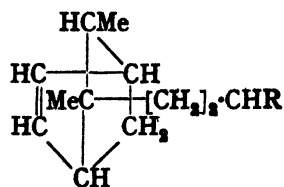
As is well known, the *cyclo*propane ring in α-santalol readily undergoes fission, and it appeared to us that if tetrahydro-α-santalol were prepared by hydrogenation of both the ethylenic linkage and the *cyclo*propane ring a direct comparison with tetrahydro-β-santalol would be possible. Attempts to reduce α-santalol catalytically resulted only in the formation of a saturated hydrocarbon, water being eliminated (compare Semmler and Risse, *Ber.*, 1913, 46, 2306). A comparison of derivatives of the two alcohols was, however, successfully effected by an indirect method.

α-Santalol is converted by thionyl chloride in pyridine solution into *α-santalyl chloride*, which on oxidation with potassium permanganate in acetone solution yields mainly tri*cyclo*ekasantalic acid together with a small quantity of a chloro-ketone, and with ozone it yields formaldehyde. The formation of tri*cyclo*ekasantalic acid is to be expected from (IV; R = Cl), but the production of formaldehyde and a chloro-ketone suggests the presence of the isomeride (V; R = Cl) or of (VI; R = Cl) formed by an anionotropic change.

$C_{11}H_{17}$·CH:CMe·CH₂R $C_{11}H_{17}$·CH₂·C(:CH₂)·CH₂R $C_{11}H_{17}$·CHR·CMe:CH₂
(IV.)   (V.)   (VI.)

(R = Cl or CH₂·CO₂H)
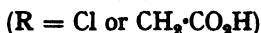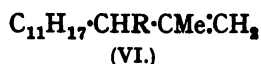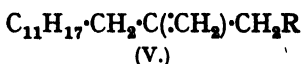
Condensation of the chloride with ethyl sodiomalonate and hydrolysis of the resulting *ester* gave α-*santalylmalonic acid*, m. p. 120—121°, the structure of which is discussed on p. 311. α-*Santalylacetic acid*, prepared by elimination of carbon dioxide at 160—180°, yields on oxidation with potassium permanganate in alkaline solution a liquid keto-acid, $C_{16}H_{24}O_3$, which does not react with sodium hypobromite at 0°, but at 28° it yields a monobasic acid, $C_{13}H_{20}O_2$, with the loss of three carbon atoms. This reaction excludes (VI; R = CH₂·CO₂H) as a representation of the acetic acid, since an acid of this structure would yield a substituted succinic acid on oxidation. It follows, therefore, that the keto-acid must be γ-keto-ε-teresantalylhexoic acid (VII), and its oxidation product β-teresantalyl-propionic acid (VIII), α-santalylacetic acid being (V; R = CH₂·CO₂H) (compare p. 311).

(VII.) $C_{11}H_{17}$·CH₂·CO·CH₂·CH₂·CO₂H $C_{11}H_{17}$·CH₂·CO₂H   (VIII.)

By the catalytic hydrogenation of α-santalylmalonic acid the dihydro-acid was prepared ; this on elimination of carbon dioxide yielded *dihydro-α-santalylacetic acid* (IX), from which, by the action of hydrogen bromide in acetic acid at 100°, a *hydrobromide* was obtained. This by reduction with sodium and alcohol gave tetrahydrosantalylacetic acid, characterised by its crystalline p-*bromophenacyl* and *diphenacyl* derivatives. This acid must be
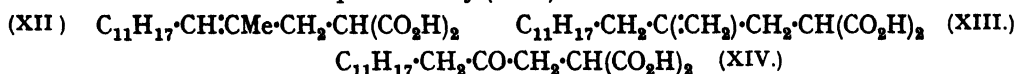
either (X) or (XI), since the fission of the bonds *a* and *b* in (IX) leads to products which are structurally identical but have enantiomorphous configurations (XI).

$$
\begin{array}{ccc}
\text{CMe} & \text{CMe} & \text{CHMe} \\
\text{(a)}\diagup \mid \diagdown\text{(b)} & \diagup\mid\diagdown & \diagdown \\
\text{HC———CH} & \text{H}_2\text{C———CH}_2 & \text{H}_2\text{C———CH} \\
\mid\text{MeC——}\mid\text{[CH}_2]_3\text{·CHMeR} & \mid\text{MeC——}\mid\text{[CH}_2]_3\text{·CHMeR} & \mid\text{MeC——}\mid\text{[CH}_2]_3\text{·CHMeR} \\
\text{H}_2\text{C}\quad\mid\quad\text{CH}_2 & \text{H}_2\text{C}\quad\mid\quad\text{CH}_2 & \text{H}_2\text{C}\quad\mid\quad\text{CH}_2 \\
\diagdown\mid\diagup & \diagdown\mid\diagup & \diagdown\mid\diagup \\
\text{CH} & \text{CH} & \text{CH} \\
\text{(IX.)} & \text{(X.)} & \text{(XI.)}
\end{array}
$$

(R = ·CH$_2$·CH$_2$·CO$_2$H)
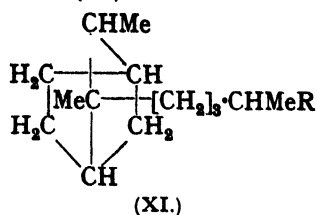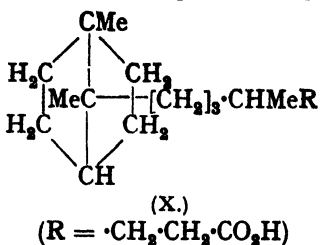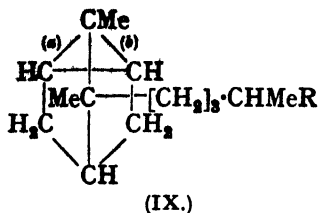
Since it has been shown synthetically by Hasselström (*J. Amer. Chem. Soc.*, 1931, **53**, 1097) that dihydroteresantalic acid, prepared by the fission of the *cyclo*propane ring in teresantalic acid with hydrogen chloride and subsequent reduction with sodium and alcohol, is identical with π-apocamphoric acid, it may reasonably be assumed that tetrahydro-santalylacetic acid is represented by (X).

In an analogous manner we have prepared from β-santalol β-*santalylmalonic acid*, m. p. 99—101°, which after catalytic hydrogenation and elimination of carbon dioxide, gives a tetrahydrosantalylacetic acid identical with that prepared from α-santalol as shown by the melting points of the *p*-bromophenacyl and diphenacyl derivatives. It follows that β-santalol, which yields acetylcarbinol on ozonolysis, must be represented by (II), since no other position for the second ethylenic linkage in the ring is possible without contravening the Bredt rule. The possibility of both ethylenic linkages being situated in the side chain is excluded by the facts that the alcohol cannot be reduced with sodium and alcohol and the molecular refraction is normal.

We must revert here to a consideration of the structure of α-santalylmalonic acid. This acid, which is highly crystalline and apparently homogeneous, provided results of considerable interest on oxidation. With ozone it yields exclusively tri*cyclo*ekasantalic acid, no formaldehyde being formed. This result implies the presence of the ethylenic linkage in the 3 : 4-position (XII). If, however, the acid is oxidised with potassium per-manganate in alkaline solution, the keto-acid (XIV) is obtained. Tri*cyclo*ekasantalic acid, which is readily isolable owing to its volatility in steam, could not be detected; the malonic acid would then be represented by (XIII).

(XII) $\quad$ C$_{11}$H$_{17}$·CH:CMe·CH$_2$·CH(CO$_2$H)$_2$ $\qquad$ C$_{11}$H$_{17}$·CH$_2$·C(:CH$_2$)·CH$_2$·CH(CO$_2$H)$_2$ $\quad$ (XIII.)

C$_{11}$H$_{17}$·CH$_2$·CO·CH$_2$·CH(CO$_2$H)$_2$ $\quad$ (XIV.)

These results, apparently unequivocal, appear to be mutually contradictory. Here is provided a clear example of the difficulty, which has for some time been familiar in terpene chemistry, of interpreting oxidation experiments in cases where the groups –C$\diagup^{\text{C}}_{\diagdown\text{C}}$ and

C:C$\diagup^{\text{C}}_{\diagdown\text{C}}$ are involved, since products arising from both Δ^{αβ}- and Δ^{βγ}-forms are frequently obtained. Of particular interest is the recent work of Kuhn and Roth (*Ber.*, 1932, **65**, 1285), who have estimated quantitatively, by means of ozone, followed by potassium permanganate, the acetone formed on oxidation of a number of substances considered to contain the *iso*propylidene group. They find in general that it amounts to only 60—90% of the calculated quantity, and oxidation with potassium permanganate alone yields still less. These authors discuss in particular the two forms of dehydrogeranic acid, which, like α-santalylmalonic acid and unlike the majority of substances examined, is crystalline. Cahn, Penfold, and Simonsen (*J.*, 1931, 3134) have reported that permanganate oxidation of dehydrogeranic acid yields both acetone and formic acid. Kuhn and Roth on the basis of optical properties consider this acid to be homogeneous and with regard to the oxidation state : " Dann lässt sich die Annahme nicht vermeiden, dass beim oxydativen Abbau durch Ozon und durch Kaliumpermanganat β-Formen [*iso*propylidene] teilweise die Spaltungs-produkte von α-Formen [*iso*propenyl] liefern können."

This view, equally with its opposite that substances behaving in this manner are in actuality inseparable mixtures (compare Simonsen, " The Terpenes," Vol. I, pp. 59 et seq.), seems now to be scarcely sufficient. It must be conceded that in α-santalylmalonic acid, and presumably therefore in other cases, the ethylene link is mobile, either under the action of reagents or even merely on solution, and in the present state of knowledge the phenomenon is best classified as tautomerism, and the two forms are to be regarded as tautomerides.

This tautomerism is observed also in the two santalols themselves, since they yield on ozonolysis both formaldehyde and acetylcarbinol; the formulæ (I) and (II) adopted for α- and β-santalol respectively are to be interpreted therefore in this sense.

It has been pointed out by Ruzicka and Stoll (*Helv. Chim. Acta*, 1922, **5**, 928) that α-santalol (I) may be regarded as a derivative of eudalene (XV). The structure now advanced for β-santalol (II) derives it from cadalene (XVI) by fission at the dotted line and

(I.)   (XV.)

(II.)   (XVI.)
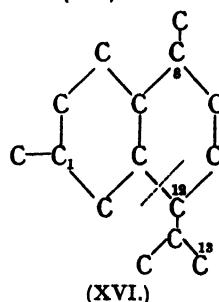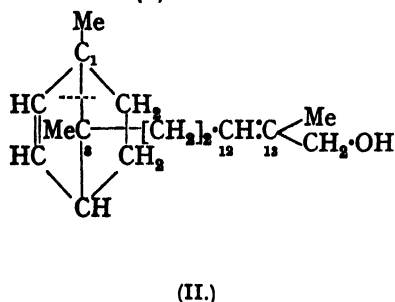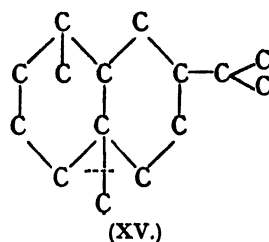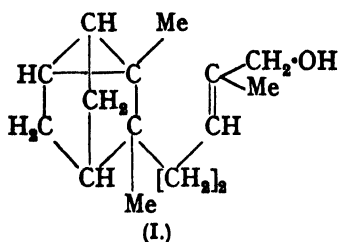
ring closure. α-Santalol (and α-santalene) can therefore equally well be considered to be a derivative of cadalene and hence occupies an intermediate position between the two parent hydrocarbons. Ruzicka and Stoll (*ibid.*, 1924, **7**, 260) have shown that the sesquiterpenic alcohols in camphor oil yield on dehydrogenation a mixture of cadalene and eudalene.

EXPERIMENTAL.

α-Santalol.

The allophanate crystallised from methyl alcohol in fine needles, m. p. 162—163°. The strychnine salt of the hydrogen phthalate separated from ethyl acetate or acetone in rosettes of well-formed prisms, m. p 144—145°, $[\alpha]_{5461}$ — 5·62° (in benzene, c 4·68).*

Oxidation with Ozone.—Ozone was passed through a solution of α-santalol in ethyl acetate cooled in ice, and the issuing gases were led through water. No formaldehyde was detected in the wash water in this experiment, but in other experiments carried out under apparently identical conditions formaldehyde was formed in considerable quantity. The ethyl acetate was removed under diminished pressure, and the product decomposed by boiling with water. After extraction with ether, acetylcarbinol was identified in the aqueous solution by preparation of the 2 : 4-dinitrophenylosazone, decomp. 300° after recrystallisation from nitrobenzene (compare Ingold, Pritchard, and Smith, J., 1934, 83), which gave a deep violet colour on warming with sodium hydroxide, and by the phenylosazone, m. p. 143—144°. The residue from evaporation of the ethereal extract was suspended in water, neutralised with potassium carbonate,

* Rotations were observed in a 1 dm. tube, except those followed by " (mic.) ", for which a ½ dm. micro-tube was used.

and extracted with ether. On acidification of the aqueous solution, tri*cyclo*ekasantalic acid, m. p. 74—75°, was obtained. Evaporation of the ethereal extract yielded an oil, from which tri*cyclo*ekasantalal semicarbazone was prepared, m. p. 163—164° (Semmler and Bode, *Ber.*, 1907, **40**, 1136, give *ca.* 156°) (Found : C, 66·4; H, 8·6. Calc. : C, 66·4; H, 8·9%).

α-Santalyl Chloride.—To a solution of the alcohol (33·3 g.) in pyridine (12 g.) cooled in ice and stirred mechanically, thionyl chloride (18·5 g.) was added gradually. The mixture was kept in ice for 15 minutes and then heated at 100° for 30 minutes. The brown reaction mixture was poured on ice, the oil extracted with ether, and the extract washed successively with dilute sulphuric acid, sodium carbonate solution, and water. Removal of the solvent from the dried solution (calcium chloride) gave an oil (32 g.), b. p. 155—158°/14 mm., $n_D^{20.5°}$ 1·5042, $\alpha_{5461} + 7·6°$ (mic.) (Found : Cl, 15·3. $C_{15}H_{23}Cl$ requires Cl, 14·9%).

Oxidation of α-Santalyl Chloride.—(i) *With potassium permanganate.* To the chloride (5·5 g.) in acetone (50 c.c.), potassium permanganate (7·5 g.) was added gradually, the solution being cooled by ice and mechanically stirred. The oxidation was complete in 3 hours. The acetone solution was filtered, the manganese dioxide sludge well washed with acetone, and the filtrate (A) reserved. The manganese dioxide was suspended in water, and sulphur dioxide passed until the dioxide was dissolved; a gummy acid remained in suspension. This was collected, dissolved in aqueous sodium hydroxide, a trace of insoluble oil removed by extraction with ligroin, the alkaline filtrate acidified, and the semi-solid acid which separated dissolved in ether. Removal of the solvent left an acid (3·3 g.), which crystallised from acetic acid (50%) and then had m. p. 76—77° both alone and after admixture with authentic tri*cyclo*ekasantalic acid. The filtrate (A) left on evaporation of the acetone a lachrymatory oil (0·7 g.), b. p. 150—160°/17 mm., which contained chlorine and reacted with carbonyl-group reagents. No crystalline derivatives could, however, be prepared.

(ii) *With ozone.* Oxidation with ozone in ethyl acetate gave a considerable quantity of formaldehyde (dimedone test). The other products of the oxidation were not investigated.

Ethyl α-Santalylmalonate.—To ethyl sodiomalonate (ethyl malonate, 16·4 g.; sodium, 2·3 g.) in alcohol (50 c.c.), α-santalyl chloride (24 g.) was added gradually with cooling. Sodium chloride rapidly separated and after 1 hour the mixture was heated on the water-bath for a further hour. The cooled neutral solution was poured into water, the oil which separated dissolved in ether, the solution dried, and the solvent evaporated. After a small quantity of unchanged ethyl malonate had passed over, the condensation product distilled at 180—220°/13 mm. and on redistillation *ethyl α-santalylmalonate* was obtained as a colourless oil, b. p. 212—213°/13 mm. (Found : C, 74·5; H, 9·6. $C_{22}H_{34}O_4$ requires C, 72·9; H, 9·4%). For the preparation of the acid, the oil (16 g.) was mixed with methyl-alcoholic potassium hydroxide (KOH, 10 g.); on warming on the water-bath, a sparingly soluble potassium salt crystallised in needles. After 1 hour water was added, the alcohol evaporated, and the solution made acid; a viscid oil then separated. This was dissolved in ether, and the solution dried and evaporated. The oil, which remained, crystallised on scratching and after trituration with ligroin (b. p. 40—60°), which removed a gummy impurity, *α-santalylmalonic acid* was recrystallised from ligroin–benzene and obtained in fine needles, m. p. 120—121°, not altered by further crystallisation, $[\alpha]_{5461} + 4·7°$ (in methyl alcohol, $c = 5·25$) (Found : C, 70·8; H, 8·7. $C_{18}H_{26}O_4$ requires C, 70·6; H, 8·5%). When the acid was heated at 160—180°, elimination of carbon dioxide occurred with formation of *α-santalylacetic acid*, b. p. 188°/2 mm. (Found : C, 78·0; H, 10·2. $C_{17}H_{26}O_2$ requires C, 77·9; H, 9·9%).

Oxidation of α-Santalylmalonic Acid.—(i) *With potassium permanganate.* The acid (3·4 g.) was dissolved in aqueous sodium carbonate and to the cooled (ice) and stirred solution potassium permanganate (3%; 150 c.c.) was added, carbon dioxide being passed during the addition. The filtered solution was concentrated to a small bulk and acidified and the liquid acid which separated was extracted with ether. Evaporation of the ether left a gum, which did not solidify and was not volatile in steam. The *semicarbazone* of β-*keto-δ-teresantalylbutylmalonic acid*, after crystallisation from methyl alcohol, decomposed at 172—173° (Found : C, 58·9; H, 7·3. $C_{18}H_{27}O_5N_3$ requires C, 59·2; H, 7·4%).

(ii) *With ozone.* The acid (1 g.), in ethyl acetate (10 c.c.) cooled in ice, was ozonised. The wash water through which the issuing gases were led gave no precipitate with dimedone. After removal of the solvent, decomposition of the ozonide by boiling water yielded tri*cyclo*ekasantalic acid. No keto-acid was detected.

Oxidation of α-Santalylacetic Acid.—When the acid (7 g.) was oxidised with potassium permanganate under conditions similar to those used for the malonic acid, a small quantity (0·2 g.) of a neutral oil volatile in steam was formed. The acid obtained by the acidification of

the concentrated alkaline solution was an oil, which did not yield crystalline derivatives with the usual carbonyl reagents. When it was distilled under diminished pressure (13 mm.), water was eliminated and a neutral oil, b. p. 200—210°, was obtained which was insoluble in cold alkali but dissolved on warming. It was probably the unsaturated lactone but was not further examined. *Methyl γ-keto-ε-teresantalylhexoate*, prepared from the silver salt, was an oil, b. p. 211°/17 mm. (Found : C, 73·2; H, 9·6. $C_{17}H_{26}O_3$ requires C, 73·4; H, 9·3%). The *semicarbazone* crystallised from benzene in needles, m. p. 176—177° (Found : C, 65·1; H, 9·2. $C_{18}H_{29}O_3N_3$ requires C, 64·5; H, 8·7%). The *phenylsemicarbazone* separated from methyl alcohol in fine needles, m. p. 192—193° (Found : C, 70·5; H, 8·1. $C_{24}H_{33}O_3N_3$ requires C, 70·1; H, 8·0%). The keto-acid (5 g.) was stable to sodium hypobromite at 0°, but at 28° oxidation proceeded rapidly with deposition of a bromo-derivative, the heat of the reaction being sufficient to maintain the temperature without further warming. Acidification of the filtered alkaline solution gave an oil, which after isolation by ether was found to contain bromine. It was dissolved in aqueous sodium hydroxide and, after the addition of zinc dust (3 g.), heated on the water-bath for 3 hours. The filtered solution was acidified and the acid, now free from bromine, was a viscid oil, from which no crystalline derivatives could be prepared. The *silver* salt was an amorphous powder readily soluble in alcohol (Found : Ag, 34·5. $C_{13}H_{19}O_3Ag$ requires Ag, 34·3%). *Methyl β-teresantalylpropionate* had b. p. 140—145°/19 mm. (Found : C, 75·4; H, 10·1. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%).

Dihydro-α-santalylacetic Acid.—α-Santalylmalonic acid was hydrogenated in ethyl-alcoholic solution in the presence of palladium-norit. The dihydro-acid, obtained as a viscid oil, was converted into the acetic acid by heating at 160—180°, and the latter purified by distillation, *dihydro-α-santalylacetic acid* being obtained as a viscid colourless oil, b. p. 208—210°/15 mm. (Found : C, 77·4; H, 11·0. $C_{17}H_{28}O_2$ requires C, 77·3; H, 10·6%). The *α-aminoanthraquinonyl* derivative crystallised from methyl alcohol in terra-cotta nodules, seen under the microscope to consist of thin irregular prisms, m. p. 105—106° (sint. 94°) (Found : C, 79·4; H, 7·3. $C_{31}H_{35}O_3N$ requires C, 79·3; H, 7·5%). By the action of hydrogen bromide in acetic acid (HBr, 50%) at 100° in a sealed tube, *bromotetrahydrosantalylacetic acid* was obtained as a viscid oil (Found : Br, 20·5. $C_{17}H_{29}O_2Br$ requires Br, 23·0%). This, on reduction with sodium in ethyl-alcoholic solution, gave tetrahydrosantalylacetic acid, which was characterised by the preparation of the *p*-bromophenacyl derivative, m. p. 52—53°, and the diphenacyl derivative, m. p. 61—62°, both alone and in admixture with specimens of these derivatives prepared from the tetrahydro-acid derived from β-santalol (see p. 315).

β-Santalol.

The *allophanate* crystallised from methyl alcohol in fine needles, m. p. 159—160°, which was slightly raised on admixture with α-santalyl allophanate (Found : C, 66·6; H, 8·9. $C_{17}H_{26}O_3N_2$ requires C, 66·7; H, 8·5%). The strychnine salt of the hydrogen phthalate crystallised from ethyl acetate in prisms, m. p. 134—135°, $[α]_{5461}$ − 37·5° (in benzene; $c = 2·68$); it was indistinguishable in appearance from that of α-santalol and the m. p. of the mixture lay between that of the two constituents.

Oxidation with Ozone.—β-Santalol (1·1 g.), in ethyl acetate (10 c.c.) cooled in ice, was ozonised. The issuing gases were led through water, which at the end of the experiment contained formaldehyde (dimedone compound, m. p. 188°). The ozonide was decomposed by boiling water, and the aqueous liquid, after extraction with ether, shown to contain acetylcarbinol by preparation of the 2 : 4-dinitrophenylosazone. The ethereal extract was not further examined.

The following derivatives of β-santalol were prepared in a similar manner to those of the α-alcohol.

β-Santalyl chloride had b. p. 161°/20 mm., $n_D^{19°}$ 1·5126, $α_{5461}$ − 66·6° (Found : Cl, 15·2%). On oxidation with ozone it gave much formaldehyde.

Ethyl β-santalylmalonate was a colourless oil, b. p. 219—220°/15 mm. (Found : C, 74·0; H, 9·6%). *β-Santalylmalonic acid* crystallised from ligroin (b. p. 60—80°) in needles, m. p. 99—101°, $[α]_{5461}$ − 60·0° (in methyl alcohol, $c = 2·528$) and was somewhat more soluble than the α-acid. In admixture with the α-acid it had m. p. 107—110°. On oxidation with ozone, formaldehyde was formed.

Reduction of β-Santalylmalonic Acid.—Agitation of a solution of β-santalylmalonic acid in ethyl alcohol in the presence of a palladium-norit catalyst, with hydrogen at room temperature and atmospheric pressure, led to the absorption of rather more than one molecular proportion of

hydrogen only. The reduction was therefore completed at 3 atmospheres' pressure and at 50—60°. After filtration from the catalyst, the solution was made alkaline with sodium carbonate, and the ethyl alcohol removed. The residue was dissolved in water, extracted once with ether, acidified, and the reduced acid extracted with ether. After removal of the solvent and elimination of carbon dioxide, tetrahydro-β-santalylacetic acid had b. p. 210—213°/16 mm. The p-*bromophenacyl* derivative separated as an oil which slowly solidified when kept in the ice-box and then crystallised from methyl alcohol in thin plates, m. p. 52—53° (Found : Br, 17·0. $C_{25}H_{33}O_3Br$ requires Br, 17·4%). The *diphenacyl* derivative crystallised from methyl alcohol in leaflets, m. p. 61—62° (Found : C, 81·0; H, 8·6. $C_{31}H_{40}O_3$ requires C, 80·9; H, 8·7%).

We are indebted to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries Ltd. for grants.

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66. *Syntheses in the Sesquiterpene Series. Part II. The Condensation of Ethyl Oxalate and Tetrahydrocarvone.*

By A. E. BRADFIELD, E. R. JONES, and J. L. SIMONSEN.

FOR the synthesis of sesquiterpenes derived from eudalene, cyclic β-ketonic esters appeared likely to be of value, since they would permit of the introduction of the angular methyl group. Kötz and his collaborators (for a summary, see Kötz and Meyer, *J. pr. Chem.,* 1913, **88**, 261) have shown that these esters are conveniently prepared by the condensation of cyclic ketones with ethyl oxalate; and, as a preliminary to the use of less readily accessible ketones, the condensation of *l*-tetrahydrocarvone and ethyl oxalate has been studied. Under the conditions described on p. 316 we were unable to isolate the ketonic

   (I.)   (II.)   (III.)   (IV.)
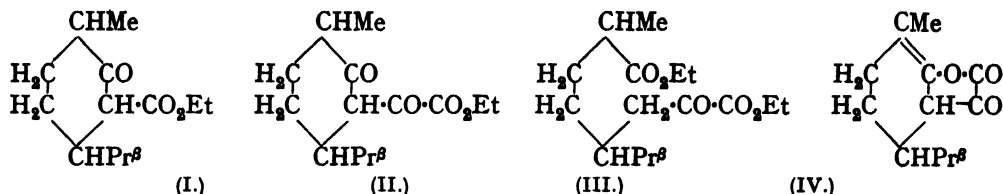
ester (I), the main product being *ethyl α-keto-ξ-methyl-γ-*iso*propylsuberate* (III), the primary condensation product (II) evidently undergoing ring fission in the presence of the sodium ethoxide. The ring fission of cyclic ketonic esters by sodium ethoxide has been observed frequently (*inter al.,* Kötz and Schüler, *Annalen,* 1906, **350**, 217; Kötz, *ibid.,* 1907, **357**, 192), the facility with which it proceeds showing considerable variation, but so far as we are aware this reaction does not as a rule proceed at low temperatures.

Ethyl α-keto-ξ-methyl-γ-*iso*propylsuberate is a mixture of the ketonic and the enolic form, and derivatives of both have been prepared. Its high molecular refraction, $[R_L]_D$ 81·16, compared with 79·44 and 80·49 calculated for the ketonic and the enolic form respectively, suggests that it exists mainly as the enol.

Oxidation of the keto-acid with hydrogen peroxide in alkaline solution gave *d-α-*methyl-δ-*iso*propylpimelic acid (compare Ruzicka and Trebler, *Helv. Chim. Acta,* 1920, **3**, 762), which was characterised by its *diamide,* m. p. 181—182°, and *di-p-toluidide,* m. p. 156—157°. When the keto-acid was warmed with concentrated sulphuric acid, ring closure occurred with the formation of the *lactone* of *Δ¹-menthen-2-ol-3-glyoxylic acid* (IV), m. p. 115°. Like other lactones of this type, it decomposed readily on exposure to the air and it was hydrolysed by alkali to the parent ketone (*l*-tetrahydrocarvone) and oxalic acid.

Kötz and Meyer (*loc. cit.,* p. 271) found that the condensation of *l*-menthone with ethyl oxalate by sodium ethoxide in ligroin solution gave as the main product the lactone of

Δ⁸-menthen-3-ol-2-glyoxylic acid. Repetition of this condensation under conditions similar to those used for *l*-tetrahydrocarvone has shown that, though this lactone is formed in small quantity, the normal condensation product, ethyl menthone-2-carboxylate (Gardner, Perkin, and Watson, J., 1910, **97**, 1770), can be readily isolated. We obtained no evidence of the occurrence of ring fission.

EXPERIMENTAL.

Condensation of l-*Tetrahydrocarvone and Ethyl Oxalate.*—To sodium ethoxide (alcohol, 100 c.c.; sodium 7·7 g.) cooled in ice–salt, a cooled mixture of *l*-tetrahydrocarvone ([α]₅₄₆₁ — 20·3°; 51 g.) and ethyl oxalate (49 g.) was added gradually. After 36 hours at 0° the deep red solution was poured on a mixture of ether, dilute sulphuric acid, and ice, the ethereal layer separated, and the aqueous solution extracted twice with ether. The combined extracts were dried, the solvent removed, and the residual oil heated under diminished pressure (20 mm.) at 130—180° (bath-temperature); vigorous evolution of gas occurred and a distillate (10·5 g.) of ethyl oxalate and *l*-tetrahydrocarvone was collected; the residue distilled at 155—160°/2 mm. (yield, 63·5 g.). When a portion of the crude ester (30 g.) was digested with methyl-alcoholic potash (400 c.c.; potassium hydroxide, 30 g.), potassium oxalate (2 g.) separated. The filtrate was distilled in steam and the oil (4 g.) obtained, b. p. 99—100°/16 mm., was shown to be *l*-tetrahydrocarvone by the preparation of the 2 : 4-*dinitrophenylhydrazone*, m. p. 133°, crystallising from alcohol in orange-red plates (Found : N, 16·4. $C_{16}H_{22}O_4N_4$ requires N, 16·8%). The alkaline solution from the steam distillation was concentrated, acidified, and extracted with ether; α-keto-ξ-methyl-γ-*iso*propylsuberic acid (23 g.) remained as a gum on removal of the solvent. The *silver* salt was an amorphous solid (Found : Ag, 47·6. $C_{12}H_{18}O_5Ag_2$ requires Ag, 47·2%). The *ethyl* ester (alcohol–sulphuric acid) was a faintly yellow oil, b. p. 148·5/1·4 mm., $d_{25}^{25°}$ 1·003, $n_D^{25°}$ 1·4548, [α]₅₄₆₁ + 7·7 (Found : C, 64·3; H, 9·6. $C_{16}H_{28}O_5$ requires C, 64·0; H, 9·3%); it gave an intense purple coloration with alcoholic ferric chloride, was readily soluble in sodium hydroxide, but insoluble in sodium carbonate solution, and its 2 : 4-*dinitrophenyl-hydrazone* crystallised from alcohol in fine yellow needles, m. p. 50° (Found : C, 54·7; H, 6·8. $C_{22}H_{32}O_8N_4$ requires C, 55·0; H, 6·7%). The *acetyl* derivative, prepared by digesting the ester with acetic anhydride and a drop of pyridine for 2 hours, was a colourless oil, b. p. 163°/2 mm.; it gave no colour with ferric chloride (Found : C, 63·2; H, 8·7. $C_{18}H_{30}O_6$ requires C, 63·2; H, 8·8%). The *methyl* ester was an almost colourless oil, b. p. 153°/2·5 mm., which gave a violet coloration with ferric chloride (Found : C, 61·4; H, 9·1. $C_{14}H_{24}O_5$ requires C, 61·7; H, 8·8%).

Oxidation of α-*Keto-*ξ-*methyl-*γ-isopropylsuberic Acid with Hydrogen Peroxide.*—To a solution of the keto-acid (6 g.) in sodium hydroxide (15 c.c.; sodium hydroxide, 2·5 g.) (ice) hydrogen peroxide (100-vol., 3·5 c.c.) was gradually added. After the vigorous reaction had ceased, the mixture was warmed on the water-bath, cooled, acidified, and extracted with ether; α-methyl-δ-*iso*propylpimelic acid (5·4 g.), b. p. 186—188°/1·5 mm., [α]₅₄₆₁ + 12° (in ethyl alcohol; c = 6·2), was obtained as a faintly yellow oil. The *diamide* crystallised from water in needles, m. p. 181—182° (Found : C, 61·5; H, 10·5. $C_{11}H_{22}O_2N_2$ requires C, 61·7; H, 10·3%), and the *di-p-toluidide* from dilute alcohol in lustrous plates, m. p. 156—157° (Found : C, 75·8; H, 8·8. $C_{25}H_{34}O_2N_2$ requires C, 76·1; H, 8·6%).

Lactone of Δ¹-*Menthen-2-ol-3-glyoxylic Acid* —The keto-acid mixed with ten times its weight of concentrated sulphuric acid was heated at 80—85° for 10 minutes, and the cooled solution poured on ice. The brownish-green solid that separated was collected and dissolved in warm aqueous ammonia (d 0·880); on cooling, the ammonium salt crystallised in long prisms which decomposed on exposure to the air. After two recrystallisations from aqueous ammonia, the salt was decomposed with hydrochloric acid and the *lactone* was collected and thrice crystallised from dilute alcohol (charcoal), being obtained in long prisms, m. p. 115°, [α]₅₄₆₁ + 104° (in alcohol; c = 1·25). The lactone decomposed somewhat rapidly on exposure to the air, but could be kept for weeks in an evacuated desiccator [Found : C, 69·5, 69·3; H, 7·7, 7·9; *M* (Rast), 212. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%; *M*, 208]. The 2 : 4-*dinitrophenylhydrazone* crystallised from dilute alcohol in small orange-red prisms, decomp. 95° (Found : C, 53·5; H, 5·7. $C_{18}H_{20}O_6N_4,H_2O$ requires C, 53·2; H, 5·4%). When digested with aqueous sodium hydroxide, the lactone decomposed with formation of *l*-tetrahydrocarvone (2 : 4-dinitrophenyl-hydrazone) and oxalic acid.

Condensation of l-*Menthone and Ethyl Oxalate.*—*l*-Menthone (α₅₄₆₁ — 23°; 15·4 g.) was condensed with ethyl oxalate under conditions similar to those used for the condensation of

l-tetrahydrocarvone. Fractional distillation of the product readily resolved it into two fractions, (i) — 130°/3 mm. and (ii) 165—195°/3 mm. From the lower-boiling fraction, ethyl menthone-3-carboxylate, b. p. 136—137°/9 mm., d_4^{20} 0·996, n_D^{20} 1·4660, $[\alpha]_{5461}$ + 44·2°, was isolated (Found: C, 69·1; H, 9·5. Calc.: C, 69·0; H, 9·7%). The higher-boiling fraction partly crystallised on keeping; the solid, after being washed with ligroin (b. p. 40—60°), crystallised from ligroin (b. p. 60—80°) in needles, m. p. 138° (softening at 100°) (Kötz and Meyer give m. p. 142·5°), $[\alpha]_{5461}$ + 12° (in alcohol; $c = 1·8$) (Found: C, 69·2; H, 7·9. Calc.: C, 69·2; H, 7·7%). As observed by Kötz and Meyer, the lactone decomposed on exposure to the air, but it was stable in a low vacuum. With alcoholic ferric chloride it gave a green colour, which changed through brown to red on keeping. When digested with alkali it gave menthone (2 : 4-dinitrophenylhydrazone, m. p. 144° alone and in admixture) and oxalic acid. It differed from the isomeric lactone derived from *l*-tetrahydrocarvone in being readily soluble in sodium carbonate solution.

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67. *Reactivity of* peri-*Substituted Naphthalenes. Part III. Further Synthetic Reactions of* 8-*Halogeno-*1-*naphthoic Acids.*

By H. GORDON RULE and H. MCNEILL TURNER.

THE reactivity of the halogen atom in 8-bromo-1-naphthoic acid is attested by the ease with which the compound may be converted, with the aid of copper-bronze catalyst, into alkoxy- and aryloxy-naphthoic acids, naphtholactone, and naphthastyril (Rule and Barnett, J., 1932, 2728; Rule and Brown, J., 1934, 137). As the bromo-acid is now obtainable in excellent yield from commercial naphthalic acid, its use in other syntheses of this type has been studied.

Among nitrogen derivatives it was found that sodioanilide reacted with 8-bromo-naphthoic acid to form N-*phenylnaphthastyril* (I). 8-Bromo-4 : 5-dinitronaphthoic acid
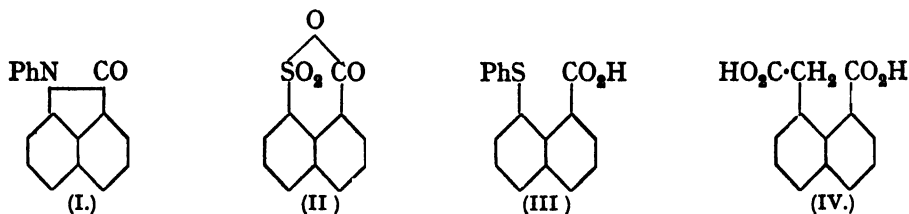
also reacted under pressure with ammonia to give 4 : 5-*dinitronaphthastyril*. The more basic compounds methylamine and piperidine, however, could not be brought into reaction with bromonaphthoic acid under any of the conditions employed, the only product obtained in the case of methylamine being a small amount of dinaphthyldicarboxylic acid, formed by the removal of bromine from two molecules of the acid.

Aqueous sodium bisulphite rapidly converted the bromo-acid into the corresponding sulphonic derivative, which was most conveniently treated with concentrated sulphuric acid and isolated as *naphthalene-*1 : 8-*carboxysulphonic anhydride* (II). This compound has been described in a patent by Cassella, G.m.b.H. (*Cent.,* 1927, II, 742), who obtained it from 8-aminonaphthalene-1-sulphonic acid by way of the cyano-derivative. The yields by the latter method are, however, poor owing to the preferential formation of naphtha-sultone from the diazonium salt. No reaction was observed when the bromo-acid was heated with aqueous sodium hydrosulphide, probably owing to the removal of the copper catalyst as sulphide. The use of sodium thiophenoxide, however, led to the formation of *phenyl* 8-*carboxy-*1-*naphthyl sulphide* (III). This compound was subsequently oxidised by hydrogen peroxide to the *sulphoxide,* which was resistant to further oxidation.

Earlier attempts to condense bromonaphthoic acid with sodiomalonic ester having failed (Rule and Barnett, *loc. cit.*), advantage was taken of the recent preparation of 8-iodonaphthoic acid from naphthastyril (Goldstein and Francey, *Helv. Chim. Acta*, 1932, **15**, 1364) to make use of the more reactive iodo-compound. In this way *homonaphthalic acid* (IV) was isolated in small yield. Here also part of the iodo-acid lost halogen with formation of the corresponding dinaphthyldicarboxylic acid.

EXPERIMENTAL.

4 : 5-Dinitronaphthastyril.—A solution of 2 g. of 8-bromo-4 : 5-dinitro-1-naphthoic acid (Rule, Pursell, and Brown, J., 1934, 170) in 30 c.c. of concentrated aqueous ammonia was heated with 0·04 g. of copper bronze, 0·04 g. of potassium chlorate, and 0·5 g. of ammonium nitrate (cf. Rule and Brown, *ibid.*, p. 137) in a glass-lined autoclave at 140—150° for 1 hour. The dark crystalline material was filtered off, washed with water, and recrystallised from glacial acetic acid, giving orange needles, m. p. 307—308°. Yield, 0·6 g.; 39% of the theoretical (Found : N, 16·1. $C_{11}H_5O_5N_3$ requires N, 16·2%).

N-*Phenylnaphthastyril.*—This was obtained by heating for 4 hours at 140° a mixture of 2 g. of 8-bromo-1-naphthoic acid, 1 g. of copper bronze, and a solution of 0·5 g. of sodium in excess of aniline. On pouring into water, a brown oil was formed, which solidified when the aniline was completely removed with acid. Two crystallisations from ligroin gave 0·5 g. of yellow needles (26% yield), m. p. 104—105° (Found : N, 5·6. $C_{17}H_{11}ON$ requires N, 5·7%). The *phenylnaphthastyril* is moderately easily soluble in the usual organic solvents and in hot concentrated hydrochloric acid. It dissolves in hot, but not in cold, aqueous sodium hydroxide, thus resembling naphthastyril.

8-Bromo-1-naphthanilide, prepared from the acid by use of thionyl chloride, followed by aniline, was found to be dimorphous, separating from benzene in long, fine, colourless needles, m. p. 125—126°, and from alcohol or ligroin in short thick prisms, m. p. 146—147°. Goldstein and Francey (*Helv. Chim. Acta*, 1932, **15**, 1364) record m. p. 151° (from alcohol) (Found : N, 4·4. Calc. for $C_{17}H_{12}ONBr$: N, 4·4%). A mixture of the two forms melted at 145—146°, a slight physical change unaccompanied by fusion occurring at 126°. The compound gave no appreciable yield of phenylnaphthastyril on being heated with copper bronze for 2 hours at 180°.

Naphthalene-1 : 8-carboxysulphonic Anhydride.—A solution of 2 g. of 8-bromo-1-naphthoic acid and 4 g. of sodium bisulphite in 15 c.c. of water was treated with 0·2 g. of copper bronze and boiled under reflux for 4 hours; it was then filtered and evaporated almost to dryness.* Cold concentrated sulphuric acid (about 20 c.c.) was added to the cold product till the whole was uniformly brownish-purple, the temperature rising to about 80°. After cooling, the addition of water threw out a white precipitate—the inorganic material being dissolved. The solid was filtered off, washed, and crystallised from a mixture (1 : 1) of water and glacial acetic acid. The *anhydride* formed colourless prisms, m. p. 152—153°. Yield, 0·85 g. (46%). It is soluble in alcohol and benzene, less soluble in ligroin and carbon tetrachloride (Found : S, 13·6. $C_{11}H_6O_4S$ requires S, 13·7%).

Phenyl 8-Carboxy-1-naphthyl Sulphide.—To 2 c.c. of thiophenol was added 0·5 g. of sodium, and the mixture heated to form sodium thiophenoxide. Thereafter, 5 g. of sodium 8-bromo-1-naphthoate, 0·5 g. of copper bronze, and 30 c.c. of xylene were added and the mixture was boiled under reflux for 40 hours, being vigorously shaken at intervals to break up the particles in suspension. The mixture was cooled, filtered, and extracted with sodium hydroxide. The aqueous layer was separated, and the excess of thiophenol oxidised to diphenyl disulphide by passing air through the solution. Insoluble disulphide was filtered off, and the filtrate acidified with hydrochloric acid. After standing over-night, the sticky material was extracted with hot water (400 c.c.) until hard and free from halogen. It then crystallised from ligroin in prisms, m. p. 131—132° (2 g., 35% yield). The *acid* is sparingly soluble in hot alcohol and ligroin, and in cold acetone, benzene, ether, chloroform and glacial acetic acid (Found : S, 11·4. $C_{17}H_{12}O_2S$ requires S, 11·4%).

Phenyl 8-Carboxy-1-naphthyl Sulphoxide.—A solution of the above sulphide in glacial acetic acid (2 g. in 15 c.c.) was heated on the steam-bath, and an equal volume of hydrogen peroxide (" 20 vol.") added slowly. After ¼ hour a white crystalline solid began to deposit, and heating was continued for a further ¼ hour. The solid was filtered off and recrystallised from aqueous

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* Better yields (85%) were subsequently obtained by boiling the dried salts for 4 hours with thionyl chloride, distilling off the reagent, and extracting the residue with benzene.

acetic acid (1 : 1), yielding 1·5 g. of colourless hexagonal plates (71% of the theoretical), m. p. 200—201°. The *sulphoxide* is fairly readily soluble in hot chloroform and in cold acetone, alcohol and acetic acid, but less soluble in hot ligroin, benzene and ether. It is insoluble in hot concentrated hydrochloric acid (Found : S, 10·6, 10·7; *M*, by titration with standard alkali, 295, 297. $C_{17}H_{12}O_3S$ requires S, 10·8%; *M*, 296. The sulphone, $C_{17}H_{12}O_4S$, requires S, 10·3%; *M*, 312). The customary method of preparing a sulphoxide with hydrogen peroxide in the cold (18 hours) yielded a mixture containing only a small amount of sulphoxide; a more vigorous oxidation of the sulphoxide in glacial acetic acid solution at 100° (3 hours) gave an oily mixture, which on purification from ethyl acetate gave only a trace of solid material, m. p. 197—198°. Mixed with the sulphoxide, this melted at 182—185°; it was possibly the sulphone, but could not be isolated in sufficient quantity for analysis, despite variations in the conditions and the use of other reagents.

Homonaphthalic Acid.—8-Iodo-1-naphthoic acid was prepared from naphthastyril (Rule and Brown, J., 1934, 137) by the method of Goldstein and Francey (*loc. cit.*), in 29% yield. To 0·5 g. of sodium dissolved in 5 c.c. of absolute alcohol was added 2 g. of iodonaphthoic acid, 0·2 g. of copper bronze, and 20 c.c. of ethyl malonate. The mixture was heated for 8 hours in an oil-bath at 120° and rendered alkaline, the excess of malonic ester removed in ether, and the aqueous layer acidified. The red oily precipitate was hydrolysed by boiling with sodium hydroxide for 1½ hours and then acidified. The red mass was extracted with 60 c.c. of chloroform, giving a red solution and leaving a brown insoluble powder (0·4 g.). On boiling the powder with benzene, filtering, and recrystallising the solid residue twice from ethyl acetate, it gave colourless plates of *homonaphthalic acid* (0·05 g.), m. p. 213—214° (decomp.) Mixed with 8-ethoxy-1-naphthoic acid (m. p. 210—211°), it melted at 194—196°. Homonaphthalic acid is practically insoluble in hot benzene, ligroin, or chloroform; but is moderately easily soluble in cold alcohol, ether, ethyl acetate and acetic acid (Found : C, 67·4; H, 4·3. $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·4%). *peri*-Carboxynaphthylmalonic acid, $C_{14}H_{10}O_6$, requires C, 61·3; H, 3·7%).

On concentration of the above-mentioned chloroform mother-liquors a reddish powder was deposited (0·1 g.), soluble in sulphuric acid to a red-brown solution, turning green on warming. This was identified as carboxybenzobenzanthrone (an intermediate product in the formation of anthanthrone from 8 : 8'-dinaphthyl-1 : 1'-dicarboxylic acid) by mixed m. p. with an authentic specimen (Cassella, G.m.b.H., *Cent.*, 1928, I, 2311).

68. *Optical Resolution of Phenyl 8-Carboxy-1-naphthyl Sulphoxide. The Prediction of Restricted Rotation in* peri-*Substituted Naphthalenes.*

By H. GORDON RULE and H. McNEILL TURNER.

THE existence of stereoisomerism due to restricted rotation has usually been predicted in one of two ways : by the " molecular diagram " method of Mills and Elliott (J., 1928, 1291) and Lesslie and Turner (J., 1932, 2021), in which the atoms are represented as spheres of known radii drawn to scale, or the trigonometrical method of Adams (*J. Amer. Chem. Soc.*, 1930, **52**, 1200), which allows a calculation of the " interference value " by which two groups overlap. Both of these methods are open to criticism, but both have been successfully used for compounds of the diphenyl series. In an attempt to obtain closer concordance between the calculated and the experimental conclusions, Sidgwick (*Ann. Reports*, 1932, **29**, 70; 1933, **30**, 119) has advocated the assumption of an interference envelope around a carbon atom amounting to about 0·5 Å. in extent, although Kleiderer and Adams (*J. Amer. Chem. Soc.*, 1933, **55**, 4220) regard this estimate as excessive. On general grounds it would appear probable that an additional factor varying with the electronic structures of the atoms or groups concerned also enters into the problem.

Unfortunately the above methods are of questionable value when applied to *peri*-substituted naphthalenes, presumably because the distance between the *peri*-carbon

atoms is not known with sufficient accuracy. Thus the optical stability of the benzene-sulphonyl derivative of 8-nitro-1-naphthylglycine studied by Mills and Elliott proved to be less than had been anticipated from the interference diagram, in which no additional envelope had been assumed. Similarly Steiger (*Bull. Soc. chim.*, 1933, **53**, 1249) has prepared the isomeric compound (I), and by using the envelope method of Sidgwick predicted the existence of comparatively stable, optically active forms. He was not able to resolve the compound, however, nor to detect any mutarotation of the alkaloid salts.

In the present instance it has been found that phenyl 8-carboxy-1-naphthyl sulphoxide (II) is readily resolvable into highly active enantiomerides, having $[\alpha]_{5461}^{20°} + 605°$ (in acetone). By using the active acid it was considered possible that the fixed centre of asymmetry in the sulphoxide group might result in preferential stabilisation of one of the isomeric forms arising from the restricted rotation of the *peri*-substituents, and so render this type of isomerism the more easily detected.

No definite information could be found in the literature concerning the valency angles in the sulphoxide group, but Bergmann (*Ber.*, 1932, **65**, 457) has deduced values for the sulphone group from dipole moment measurements. Assuming that the angles so obtained also hold without modification for the sulphoxide, it follows that the bonds joining sulphur to the phenyl and naphthyl nuclei enclose an angle of 109°, and those linking sulphur to oxygen and naphthalene make an angle of approximately 112°. On this basis and adopting the atomic dimensions used by Lesslie and Turner (*loc. cit.*) the resulting molecular diagram shows that neither the oxygen atom of the sulphoxide group nor the carbon atom of the benzene ring attached to sulphur is capable of clearing the carboxylic carbon atom. It thus follows that definite evidence of restricted rotation is to be anticipated without any assumption of an atomic envelope. Even if the above angles are given the improbably high value of 120°, the diagram shows that the carboxylic carbon atom is practically in contact with the carbon atom of the benzene ring and that it passes within 0·2 Å. of the oxygen atom of the sulphoxide group. Experiment proved, however, that no trace of mutarotation could be observed with the alkaloid salts of the active acid, and that the free acid was unaffected by heat treatment at 100°.

<center>EXPERIMENTAL.</center>

Resolution of Phenyl 8-Carboxy-1-naphthyl Sulphoxide.—The inactive sulphoxide (see preceding paper), m. p. 200—201°, was dissolved in boiling ethyl acetate (1·12 g. in 80 c.c.), and to it was added a boiling solution of 0·8 g. of brucine in 6 c.c. of ethyl acetate. On cooling, 1·18 g. of salt were obtained, and this was resolved by continued fractionation from chloroform until a sample (0·6 g.) was obtained having $\alpha_D = + 9·62°$ ($l = 1$; $t = 20°$; $c = 3·458$). A solution of the active salt in pyridine showed no signs of mutarotation.

Liberation of the Active Acids.—A chloroform solution of the above *d*-salt was repeatedly extracted with dilute hydrochloric acid until completely free from brucine, the large volume of acid required (300 c.c.) being very noticeable (cf. Harrison, Kenyon, and Phillips, J., 1926, 2088). The chloroform was removed in a vacuum, and the *d*-acid then separated in hexagonal prisms, m. p. 200—201° (this is the same as that of the inactive material). In moist chloroform, the acid had $[\alpha]_D^{20°} = + 380·5°$ and in acetone $[\alpha]_{5461}^{20°} = + 605°$.

The *lævo*-form of the acid was obtained in a slightly less pure state by removing ethyl acetate from the mother-liquor resulting from the first crystallisation of the brucine salt. The recovered salt (0·7 g.) was decomposed as above without further purification, and yielded an acid of $[\alpha]_{5461}^{20°} = - 500°$ in acetone.

Dispersion.—The graph of $1/\alpha$ and λ^2, plotted from the figures given below, is a straight line, showing that the compound has simple dispersion over the wave-length examined.

Rotation of the d-*acid in acetone.*

$t = 20°. \quad l = 1. \quad c = 0.2000.$

λ, Å.	6563	5893	5463	4861	4358
α	+0·76°	+0·98°	+1·21°	+1·67°	+2·38°
[α]	+380°	+490°	+605°	+835°	+1190°

The above solutions of the active acid showed no perceptible mutarotation, nor was any racemisation observed when the acid was heated for 1½ hours in glacial acetic acid solution at 94°.

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69. *Kinetics of Salt-hydrate Dissociations:* $MnC_2O_4,2H_2O = MnC_2O_4 + 2H_2O.$

By BRYAN TOPLEY and MERVYN L. SMITH.

IN continuation of previous kinetic studies of salt hydrates (*Proc. Roy. Soc.*, 1931, *A*, **134**, 224; 1932, **136**, 413; *Phil. Mag.*, 1932, **14**, 1030), we have examined in detail over a range of temperature and water-vapour concentration the velocity of dissociation of manganous oxalate dihydrate.

The main interest of the results lies in the unusual dependence of the rate of dissociation upon the concentration of water vapour in the atmosphere surrounding the solid. This dependence, in reactions of the type Solid$_I$ $\rightleftharpoons$ Solid$_{II}$ + Gas, seems normally to be that the reaction velocity constant is a maximum when the concentration of gaseous product is zero and decreases continuously to zero at the equilibrium concentration. The reaction now described is an exception to this generalisation, since there is a strong acceleration of the rate by water vapour within a certain well-defined range of pressures. (The effect does not resemble the catalysis by traces of water vapour associated with the behaviour of intensively dried systems.)

EXPERIMENTAL.

The apparatus and method of experiment are similar to, and the terminology employed in this paper is the same as, those previously used (*loc. cit.*; and J., 1929, 2633). The reaction was followed by weight decrease of a sample of the hydrate contained on a light glass pan hung from a quartz-spring microbalance by means of a quartz thread descending from the micro-balance chamber into a long tube kept in a thermostat. When it was desired to remove the water molecules as efficiently as possible after they had left the solid, phosphoric oxide was placed in the tube near the solid, and permanent gas was removed by a mercury-vapour pump and a charcoal–liquid-air trap. For experiments in which the solid decomposed in an atmosphere of known water-vapour concentration, the two methods previously described in detail were used : *i.e.*, for partial pressures of water vapour up to 0·2 mm., the " flow " method with hydrogen as a carrier gas was available, and for higher pressures the " static " method, an ice or water bulb at controlled temperatures being used to maintain known water-vapour pressures. It had been found in the earlier work that the two methods agree in the overlapping range when both are available, and confirmation of this has now been obtained.

Manganous oxalate dihydrate was prepared by addition of finely divided potassium permanganate to hot oxalic acid solution. After thorough washing with boiling water, the product consists of small, white, apparently octahedral crystals, fairly even in size. From the application of Stokes's law to the rate of fall of these through their saturated solution, the radius of the equivalent spherical particle was found to be 0·0044 cm., so that a typical reaction sample of 50 mg. contains about 5×10^4 individual crystals. The low solubility prevents the growth of single crystals large enough for rate measurements. Most of the experiments were done with reaction samples taken from the same preparation, but a second preparation gave rates in excellent agreement with the first. The weight loss after complete dehydration in a stream of nitrogen at 120° corresponded accurately to the composition of the dihydrate; therefore, decomposition of the oxalate was not to be feared in the dehydration experiments, in which the crystals were not heated above 90°.

The reaction curves (wt. loss–time) obtained in a vacuum or in a constant partial pressure of water vapour are of the strongly accelerating type. Spontaneous formation of reaction centres practically does not occur at room temperatures : the crystals are stable for days in vacuum over phosphoric oxide. At 50°, dehydration becomes perceptible only after many hours, whereas at 75° a large number of reaction centres are formed in ¼ hour. It is clear, qualitatively, that the process of spontaneous nucleation of the surface has a much higher temperature coefficient than the subsequent propagation of the reaction interface. This is in agreement with the view developed in the earlier papers concerning the activation energy of interface reactions of this type.

Reactions in which the nucleation probability is small relative to the rate of propagation of the interface do not lend themselves to accurate determination of the latter, unless the crystals can be artificially nucleated at many points. Since the manganous oxalate dihydrate crystals are too small for this to be practicable by mechanical means, the following procedure was adopted with each new reaction sample : decomposition was started at 90° in vacuum, and after it had proceeded to the extent of 10—15%, a thermostat at the required reaction temperature (<90°) was substituted for the bath at 90°, and at the same time the water-vapour concentration was adjusted to the required value (in " static " experiments) or the hydrogen–water-vapour flow started (in " flow " experiments).

After approximately 20% decomposition, the rate falls slowly and then more rapidly, as a consequence of the decreasing area of reaction interface and the increasing " impedance effect " of the solid product (*loc. cit.*). To obtain a common basis for comparison of rates measured at other percentage decompositions than 20%, a set of experimental curves showing the reaction rate at different percentage decompositions was prepared, and used to reduce rates measured at percentage decompositions other than 20% back to this standard amount of decomposition. Since the " impedance effect " must vary somewhat both with temperature and with the concentration of water molecules maintained outside the decomposing crystals, a new curve is in principle required for any change in either of these parameters. In practice it was found sufficient to prepare a few such curves and to use the one most nearly corresponding to the conditions of the experiment in question. The following typical figures indicate the magnitude of the corrections involved :

Decomposition, %	18·4	20·0	27·0	36·2	42·0	47·0	57·0
Reduction factor	0·99	*1·00*	1·06	1·15	1·20	1·25	1·37

The sensitivity of the quartz-spring microbalance permitted rate measurements accurate to ± 2% within a range equal to 3% of the weight loss corresponding to complete reaction. These rates, multiplied by the appropriate factor (see above) and then divided by the initial weight of the hydrate in decigrams, gave values which we take as reaction velocity constants. The constants are arbitrary in two respects : they refer to a definite but unknown area of reaction interface, *viz.*, that produced in a 100-mg. sample of the dihydrate which has been decomposed to the extent of 20% in the standardised way explained above; and the " impedance effect " is not eliminated, but only standardised by the procedure adopted. It is probable that the velocity constants are not very seriously affected by the " impedance effect," since the decrease in rate after 20% decomposition in any one experiment is such as may feasibly be attributed mainly to the decreasing area of reaction interface; but in any case the conclusions concerning the general nature of the dependence of rate upon water-vapour concentration are not vitiated by the uncertainty as to the magnitude of this effect.

There is no evidence in the literature suggesting that a hydrate lower than the dihydrate exists. A number of runs under different conditions of water-vapour concentration and temperature were carried through until more than 90% of the combined water had been lost : no deceleration of the reaction in the neighbourhood of a hypothetical monohydrate was detectable.

The Temperature Coefficient.—Table I contains the results of experiments done by the " static " method with phosphoric oxide present in the reaction vessel. The reproducibility of velocity constants at any temperature is about ± 15%. There does not appear to be any

TABLE I.

Temp.	k, exp.	k, interp.	H₂ (mm. Hg).	Temp.	k, exp.	k, interp.	H₂ (mm. Hg).
25·0°	0·00028	0·00028 ⎱ Mean of several expts.		59·0°	0·023	0·022	0·19
35·0	0·0013	0·0011 ⎰ with and without H₂.		64·8	0·034	0·040	0·40
45·2	0·0032	0·0039	0·26	69·7	0·070	0·070	nil
58·9	0·024	0·021	nil	69·7	0·060	0·070	0·29

effect arising from the presence of hydrogen, other than the conductivity effect, which decreases the self-cooling of the dissociating hydrate. The temperatures (col. 1) have been corrected : a thermal stationary state is established in which the suspended solid is slightly below the thermostat temperatures. (The calculation of this correction, at most 1°, was done as previously described; *Proc. Roy. Soc.*, 1931, *A*, **134**, 235.) It being assumed that the " impedance effect " can be neglected, the velocity constants in cols. 2 and 3 are the reaction rates (in the units defined above) under the condition that the adsorbed water molecules in the reaction zone are at the lowest concentration consistent with the interfacial nature of the reaction; this concentration cannot in principle be zero (see *Phil. Mag.*, 1932, **14**, 1080). The constants in col. 3 are obtained from the expression $\log_{10} k = 14.83 - 5479/T$, which fits the experimental points. Col. 4 records the presence or absence of hydrogen. Experiments were also made at higher temperatures, and were actually in agreement with these, but have been rejected because analysis of the solid remaining showed that, at any rate in a vacuum, phosphoric oxide sublimed on to the hydrate in detectable quantities. The activation energy is 24·3 kg.-cals. per mol. H_2O.

The Effect of Water Vapour on the Reaction Rate.—The behaviour of a sample of the hydrate suspended in a closed and initially evacuated space shows qualitatively that water vapour can retard or accelerate the net rate of decomposition according to its concentration; as the water vapour produced by the hydrate accumulates in the reaction vessel, the rate of dissociation falls and later reaches a minimum value of the order of one-thirtieth of its previous value. Only a small part of the decrease in rate of loss of weight is attributable to increasing adsorption on the amorphous solid, because the volume and pressure of the water vapour in the reaction vessel corresponded as nearly as could be estimated with the loss in weight of the hydrate. The dissociation proceeds slowly for some time, then gradually accelerates to reach a value several times larger than the minimum rate.

The quantitative dependence of rate upon water-vapour concentration has been closely examined in the range of water-vapour pressure within which the velocity constant passes through a minimum and then a maximum with increasing p_{H_2O}. The smaller partial pressures were obtained by the " flow " method, and the larger by the " static " method; in the overlapping region where rate constants were obtained by both methods, the consistence is nearly as good as that of duplicate experiments by either method. Two series of measurements were made, at 75·9° and 68·0° (Table II).

TABLE II.

p_{H_2O}, mm. Hg.	k.	Method.	p_{H_2O}, mm. Hg.	k.	Method.	p_{H_2O}, mm. Hg.	k.	Method.	p_{H_2O}, mm Hg.	k.	Method.
					(a) *Temperature* 75·9°.						
0	0·135	S	0·0240	0·030	F	0·16	0·0165	S	2·19	0·100	S
0·0042	0·122	F	0·0257	0·024	F	0·163	0·0178	F	2·19	0·111	S
0·0096	0·097	F	0·0402	0·015	F	0·21	0·033	S	2·23	0·111	S
0·0129	0·071	F	0·0510	0·012	F	0·212	0·051	F	2·54	0·102	S
0·0136	0·062	F	0·07	0·011	S	0·33	0·062	S	2·98	0·093	S
0·0141	0·060	F	0·0824	0·0093	F	0·415	0·093	S	3·81	0·084	S
0·0146	0·072	F	0·0858	0·0089	F	0·47	0·100	S	4·58	0·067	S
0·0161	0·045	F	0·09	0·0099	S	0·955	0·132	S	4·58	0·046	S
0·0201	0·040	F	0·111	0·0090	F	1·11	0·121	S	6·54	0·035	S
0·0207	0·037	F	0·125	0·0083	S	2·19	0·121	S	9·21	0·029	S
0·0209	0·039	F	0·141	0·0092	F	2·19	0·111	S	12·79	0·017	S
0·0224	0·032	F				2·19	0·114	S			
					(b) *Temperature* 68·0°.						
0	0·059	S	0·0088	0·024	F	0·0182	0·0037	S	0·161	0·0029	S
0·0044	0·041	F	0·0099	0·022	F	0·0217	0·0031	S	0·192	0·0041	S
0·0047	0·038	F	0·0108	0·013	F	0·0243	0·0025	S	0·220	0·0056	S
0·0057	0·037	F	0·0135	0·005	S	0·0305	0·0020	S	0·240	0·0063	S
0·0060	0·034	F	0·0150	0·004	S	0·0385	0·0018	S	0·277	0·0079	S
0·0077	0·020	F	0·0169	0·0077	F	0·0474	0·0016	S	0·324	0·0102	S
0·0080	0·024	F				0·127	0·0033	S			

Col. 1 gives the water-vapour pressure (in " static " experiments) or partial pressure (with hydrogen as carrier gas, in " flow " experiments) in mm. Hg. The corresponding rate constants, in the units already defined, are given in col. 2. The letters F or S indicate the " flow " or the " static " method. The temperature corrections for the crystals were negligible because of the relatively large conductivity of the hydrogen or water vapour present in these particular experiments when the rate was large; in the neighbourhood of the minimum, the cooling was in any

case small. Inspection of the data shows that the behaviour is quite complicated, in marked contrast to the other systems whose behaviour in respect of the gaseous product has been studied. The two rates at zero water-vapour pressure are calculated from the formula already given for the rate in vacuum. In spite of one or two irregularities, the main outlines of the phenomenon are quite clear: at 75·9°, the rate falls sharply with small pressures of water vapour to a minimum and then rises less sharply to a maximum about equal to the rate in a vacuum. The minimum, at $p_{H_2O} = 0·11$ mm. is very sharp; the maximum at $p_{H_2O} = 0·9$ mm. is much less sharp, but definite. The results at 68·0° are similar, but were not followed as far as the maximum. At 75·9° the rate at the minimum is 0·07 of that in a vacuum, and the water-vapour pressure is approximately 0·0014 of the equilibrium vapour pressure. The corresponding figures at 68·0° are 0·03 and 0·00082 respectively.*

DISCUSSION.

The measured reaction velocity is the net rate of escape of water molecules into the gas phase. When the dissociating hydrate is in contact with an arbitrarily fixed concentration of water vapour, we may assume that this is in equilibrium with the adsorbed water molecules on the surface of the finely divided and porous solid product,† and that this equilibrium extends also to the reaction interface. Apart from the small proportion of the original content of combined water carried by the anhydrous product in the form of adsorbed water, the measured rate is simply the algebraic sum of the different unit processes taking place in the reaction zone. It is probable that the main forces causing the adsorption are electrostatic forces between water dipoles and the ions of the anhydrous solid, and secondary forces among the dipoles themselves, oriented by the underlying ions. When the number of water molecules in the reaction zone is sufficient, an appreciable proportion of these (mobile) molecules will occupy adjacent positions (the proportion of pairs of adjacent molecules may be much larger than a purely random distribution would allow, since there may exist a substantial lateral attraction between suitably oriented molecules). The forward and the reverse chemical reaction, in which water molecules in the reaction zone pass over a potential hill from the chemically combined state to the adsorbed state, and inversely, are controlled by the heights of this hill above the two valleys. The height from the valley representing the state of chemical combination in the hydrate lattice is determined, not only by the nature of the binding in the lattice, but also by the adsorption potential on the anhydrous salt, since the molecule surmounts the hill whilst acted upon by a force directed towards the solid reaction product as well as by the restoring force towards the hydrate lattice. If the first of these is relatively important, as it must be in a reaction so definitely of the interfacial type, then the actual energy of activation for a particular water molecule will be a function of the configuration of the adsorbed molecules in the neighbouring part of the reaction zone. The existence of a minimum rate at a certain pressure of water vapour, followed by an increase to a value near the initial (vacuum) rate, indicates that, at any rate in the region of the minimum, the positive catalytic effect increases considerably more than linearly with increasing concentration of water molecules. It seems plausible to associate this with the variation (as the concentration is increased) in the number of spaces

* The whole water-vapour pressure range covered by these experiments is a comparatively small fraction of the complete range up to the saturated vapour pressure of the hydrate–anhydrous salt system. The latter amounts to approximately 78 mm. and 49 mm. at the higher and the lower temperature respectively. The vapour pressure (in mm. Hg) is approximately given by $\log_{10}p = 10·438 - 2982/T$. The system approaches equilibrium extremely slowly in a tensimeter, and this formula is derived from a single prolonged experiment at 45·20° combined with calorimetric measurements previously reported (J., 1932, 1977). The calculation of the cooling corrections was based on these measurements also.

† The assumption implied is that the desorption and adsorption processes are rapid in comparison with the dissociation of the hydrate lattice; this is very probable, since the activation energy for dissociation is in the neighbourhood of 24 kg.-cals., whereas the adsorption potential cannot exceed 8 or 9 kg.-cals., for if it were larger than this, the adsorption would tend to saturation at pressures of water vapour at which, as the reaction kinetics show, saturation is not being approached. We are, of course, assuming here that the adsorption potential is also the activation energy for the desorption process, and that the temperature-independent factor is of the same order of magnitude for the dissociation and for the desorption processes.

unoccupied by adsorbed molecules, *which are situated between occupied spaces in the reaction zone.* One possibility is that an unoccupied space, available for a molecule dissociating over the potential hill, is associated with a lower hill if it falls between two (or more) adsorbed water molecules oriented with their outer poles having the opposite sign to that presented by the escaping water molecules. With a suitable configuration the activation energy might be lowered by several kg.-cals.; at the same time, the mutual potential of oppositely oriented molecules adsorbed within range of each other's attraction will increase the activation energy required to pass from the adsorbed to the combined state; and diminish correspondingly the probability of the recombination. It does not seem extreme to suppose a change in the height of the hill of as much as 4 kg.-cals., which would correspond to an increased probability of dissociation over the hill, or a decreased probability of the reverse reaction, of over 300-fold. As the reaction zone becomes still more densely occupied, the number of spaces of any sort available to receive molecules from the hydrate lattice will decrease until finally the rates of dissociation and of recombination become equal. No quantitative development of this view is possible in the absence of knowledge of the inter-molecular and interionic distances involved; but if it is correct to attribute the (net) positive catalysis by water vapour to a modification of the activation energy as suggested, then it is to be anticipated that the whole effect will depend very much upon a suitable spacing of the positive and negative ions of the solid reaction product.

Menzies and Potter (*J. Amer. Chem. Soc.*, 1912, **34**, 1452) describe qualitatively the behaviour of the hydrate $3As_2O,5H_2O$ on dehydration, which is apparently similar to that of the $MnC_2O_4,2H_2O$. They found that at 170° the dehydration was more rapid and more thorough in the presence of 300 mm. than of 20 mm. of water vapour, and still more so than in the presence of 10 mm.

SUMMARY.

The dissociation reaction $MnC_2O_4,2H_2O = MnC_2O_4 + 2H_2O$ has been studied kinetically. Spontaneous nucleation of the surface of the crystals is comparatively infrequent at temperatures suitable for measurements of the rate of propagation of the interface, and rate measurements have been confined to samples of the hydrate nucleated at a higher temperature.

The activation energy for the dissociation in vacuum is 24·3 kg.-cals.

The rate of dissociation is a complicated function of the concentration of water vapour surrounding the solid; with increasing concentration, the rate constant at first decreases strongly, passes through a minimum, and increases strongly to a maximum of the same order of magnitude as the rate in vacuum, and then falls more slowly. The interpretation of this is discussed in general terms.

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70. *The Colouring Matters of* Drosera Whittakeri. *Part I. The Absorption Spectra and Colour Reactions of Hydroxy-naphthaquinones.*

By A. KILLEN MACBETH, J. R. PRICE, and F. L. WINZOR.

THE insectiverous plant *Drosera Whittakeri*, which is fairly widely distributed in the Adelaide Hills, contains two colouring matters deposited as reddish flakes between the outer sheaths of the small bulb attached to its single root : the bulb itself contains a pale-red sap in which only a negligible concentration of the dye is present. The principal component, $C_{11}H_8O_5$, is isolated as red plates, m. p. 192—193°, from glacial acetic acid; associated with this is a small amount of a more soluble compound, $C_{11}H_8O_4$, consisting of yellow needles, m. p. 178° : traces of the former are removed from the latter only with difficulty. Rennie (J., 1887, **51**, 371; 1893, **63**, 1083) showed that the O_5-compound formed a triacetate and was probably a trihydroxymethylnaphthaquinone : whereas the O_4-compound gave a diacetate and appeared to be a dihydroxymethylnaphthaquinone.

These compounds have now been submitted to further examination and Rennie's suggestions confirmed. For convenience it is proposed to name the O_4-compound *droserone* and the O_5-compound *hydroxydroserone*. In this paper evidence is submitted on which the constitution of the latter may be based. It appears to be 3 : 5 : 8-trihydroxy-2-methyl-1 : 4-naphthaquinone. The amount of droserone available was too small, and its purity too doubtful, to permit of a reliable deduction of its structure by the methods of absorption spectroscopy.

The difference in colour between 1 : 4- and 1 : 2-naphthaquinone (pale yellow and orange-red respectively) led early observers to assign the latter structure to highly coloured derivatives of naphthaquinone such as *iso*lapachol (Hooker, J., 1896, **69**, 1357). As the introduction of hydroxyl groups in many cases brings about a very marked change in the colour of 1 : 4-naphthaquinone, this physical characteristic is much too unreliable a guide on which to base such a conclusion (Fieser and Ames, *J. Amer. Chem. Soc.*, 1927, **49**, 2604), and evidence has since been submitted that the assumption of 1 : 2-naphthaquinone structure was quite unwarranted. Tests such as solubility in sodium bisulphite must also be applied with caution (Fieser, *ibid.*, 1926, **48**, 2925). In the simple naphthaquinones with one hydroxyl group in the quinone nucleus, two tautomeric forms, (I) and (II), may
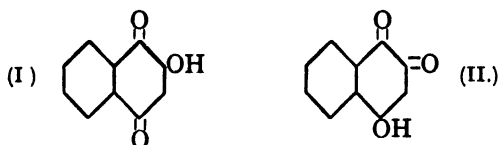
exist in equilibrium, and attempts were made to gain some definite idea of the amounts of each present by estimation of the percentages of the respective ethers that could be isolated after etherification (Miller, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 440; 1915, **47**, 1536). The results were later shown to be unreliable, for the particular ether formed was found to depend both on the nature of the alkyl group and on the reactivity of the halogen atom in the alkyl halide employed (Fieser, *loc. cit.*).

Electrode-potential measurements, on the other hand, have been applied with more success, and the results indicate that the 1 : 2-structure is very unstable (*idem, J. Amer. Chem. Soc.*, 1928, **50**, 438). If the constant of the tautomeric equilibrium of the α- and the β-form is defined by the equation $K = [\alpha\text{-form}]/[\beta\text{-form}]$, a simple thermodynamical consideration of the free energies of reduction of the two forms to the common reductant gives an expression dependent on temperature, which at 25° becomes

$$\log K = [E_0{}^\beta - E_0{}^\alpha]/0\cdot0296,$$

where $E_0{}^\alpha$ and $E_0{}^\beta$ are the normal reduction potentials of the two forms. Working values may be obtained by examining the ethers instead of the parent hydroxy-quinones (the β-form being unstable), and since $E_0{}^\alpha$ for 2-methoxy-1 : 4-naphthaquinone is 0·353 volt and $E_0{}^\beta$ for 4-methoxy-1 : 2-naphthaquinone under the same conditions is 0·433 volt, the difference (0·08 volt) substituted in the equation leads to a value of $K = 502$. In other words, in the solvent in question (37% alcohol), only 0·2% of the β-form is present in the equilibrium mixture. It is therefore very unlikely that a hydroxy-naphthaquinone with the group as a substituent in the quinone ring will exist in other than the 1 : 4-form : since hydroxydroserone contains such a group, the α-structure is thus rendered very probable, a conclusion which is supported by the absorption spectra now examined.

The spectra of representative hydroxy-naphthaquinones are reproduced in the figs. which show that the introduction of hydroxyl groups in most cases modifies the absorption of 1 : 4-naphthaquinone and 2-methyl-1 : 4-naphthaquinone which may be regarded as typical of the 1 : 4-structure : the curves of the acetates, however, revert to a form which closely resembles the simple type. On the other hand, the absorption of 1 : 2-naphthaquinone examined by Goldschmidt and Graef (*Ber.*, 1928, **61**, 1862) is markedly similar to that of 4-methoxy-1 : 2-naphthaquinone now described. One band in the spectra of these substances is not found in the case of the 1 : 4-naphthaquinone type, and may be

regarded as a criterion for the 1 : 2-structure. Since acetylated hydroxydroserone does not show such a band, but on the contrary generally resembles the 1 : 4-type, it seems
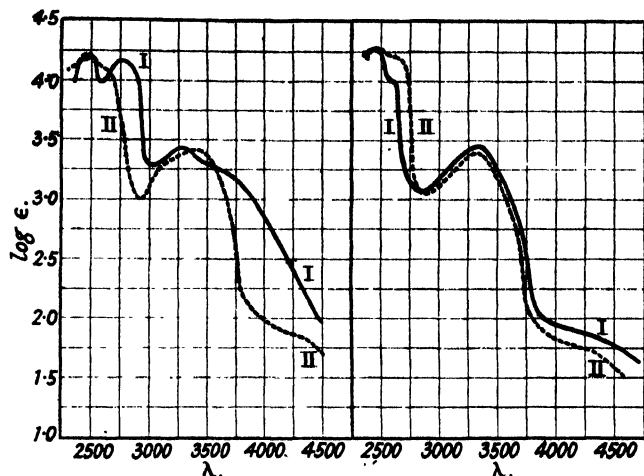
I = 2-*Hydroxy*-1 : 4-*naphthaquinone*.   I = 1 : 4-*Naphthaquinone*.
II = 2-*Acetoxy*-1 : 4-*naphthaquinone*.   II = 2-*Methyl*-1 : 4-*naphthaquinone*.
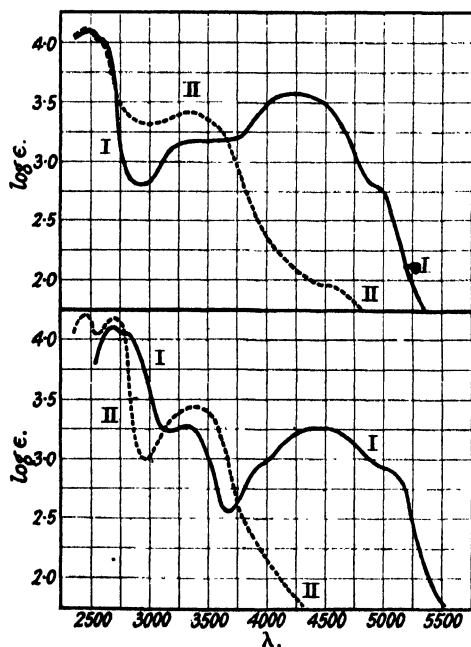
Upper curves I = *Juglone*.   *Upper curve* I = *Methoxy*-1 : 2-*naphthaquinone*.
          II = *Juglone acetate*.   *Lower curves* I = *Hydroxydroserone*.
*Lower curves* I = iso*Naphthazarin*.   II = *Hydroxydroserone triacetate*.
          II = iso*Naphthazarin diacetate*.

justifiable to infer that it possesses the latter structure : the question, however, will be discussed more fully later.

For purposes of comparison, the absorption maxima observed may be grouped into several spectral regions, and these are summarised in the tables below : the numbers

italicised indicate that an inflexion occurs at that particular wave-length instead of a band.

Baly and Stewart (J., 1906, **89**, 502, 618), as a result of a qualitative examination of a number of substituted benzoquinones, found that considerable modification in the characteristic absorption of the parent quinone occurred on substitution, and in the case of highly substituted compounds points of similarity had almost or entirely disappeared. They concluded that the effects could be explained by assuming that the substituted quinones
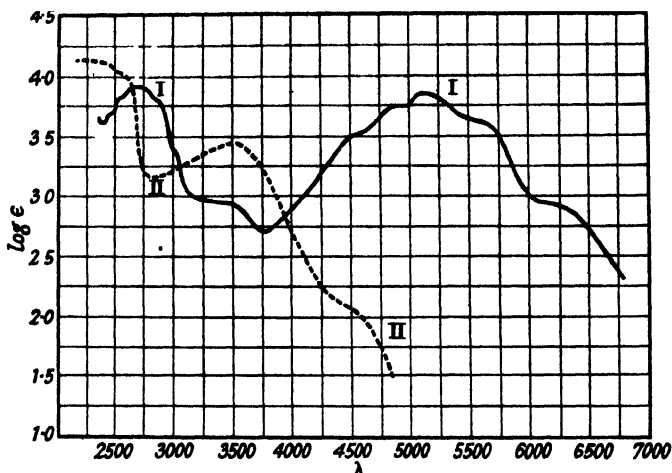
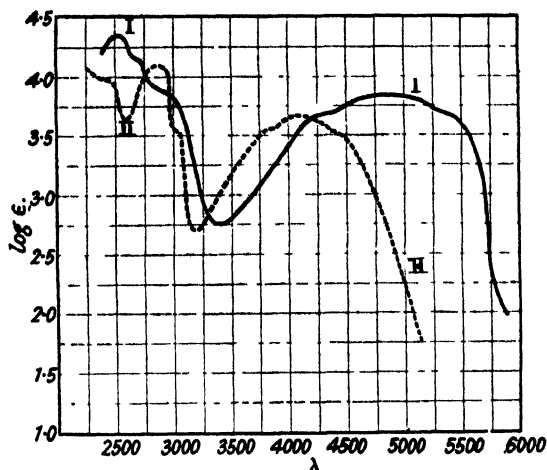I = *Naphthazarin.*   II = *Naphthazarin diacetate.*
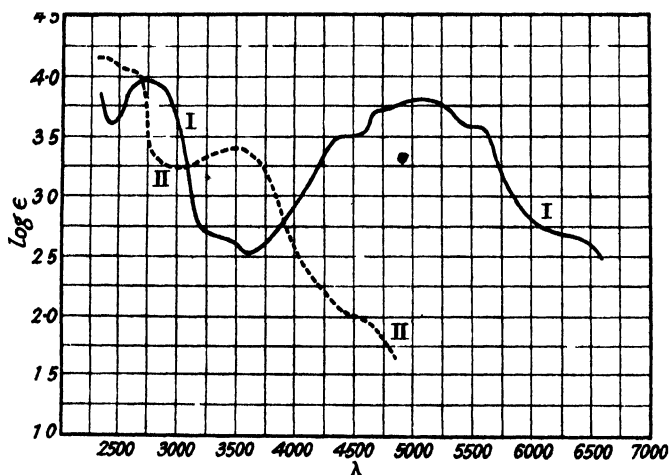
I = *Methylnaphthazarin*   II = *Methylnaphthazarin diacetate.*

were definitely of a more benzenoid character. The further suggestion, that the increasing difficulty experienced in oxime formation as substitution increases might be accounted for on this basis rather than by steric hindrance as suggested by Kehrmann (*Ber.*, 1888, **21**, 3315; *J. pr. Chem.*, 1889, **39**, 399; **40**, 257), is not altogether free from objection, but in view of Baly and Stewart's work it was thought desirable to compare the wave-lengths of the bands or inflexions in the spectra of the hydroxynaphthaquinones with the bands recorded for naphthalene and the alkylnaphthalenes by Morton and de Gouveia (J., 1934, 927) and attributed by them to the absorptive centre C_6H_5—C=C—. The naphthalene maxima are included in Table I, and although there is some apparent agreement it is

improbable that this is due to the quinone existing in the bimolecular, aroxyl, or peroxide form which is necessary to provide the C_6H_5—C=C— chromophore. The aroxyl and peroxide forms cannot be reconciled with the behaviour of the hydroxynaphthaquinones which contain hydroxyl groups in *peri*-positions to the quinone oxygens: and Goldschmidt and Graef (*loc. cit.*) have shown that in *o*-benzoquinone the amount present in the aroxyl form can only be very small indeed, and in *p*-benzoquinone even smaller. Further, comparison of the log ϵ values disclosed the fact that these are consistently higher for the hydroxynaphthaquinone bands than for the corresponding naphthalene bands: and the contention that the maxima of the former are connected with a naphthenoid structure cannot therefore be sustained.

It seems more probable that the bands in Tables I and II may be correlated with the maxima observed

I = *Naphthapurpurin.* II = *Hydroxyjuglone.*

by Morton, Hassan, and Calloway (J., 1934, 883) in the curves of benzaldehyde, acetophenone, and other aromatic aldehydes and ketones. These workers showed that the $C_6H_5\cdot CO$ group gives rise to three distinct bands; the first, of low persistence, at λ 310—320 mμ, they attributed to the $\overset{*}{C}{=}O$ group, the second at λ 280 mμ to the carbonyl group influenced by phenyl C_6H_5—$\overset{*}{C}{=}O$, and the third at λ 242 mμ to the phenyl group influenced by carbonyl $\overset{*}{C_6H_5}$—C=O. Since the $C_6H_5\cdot CO$ group is present

TABLE I.

λ 250—300 mμ.

Substance.	λ_{max}.	log ϵ.	Naphthalene. λ_{max}.	log ϵ.
2 : 5-Dihydroxy-1 : 4-naphthaquinone (Hydroxyjuglone)	*301*	3·56	302	2·54
5 : 8-Dihydroxy-1 : 4-naphthaquinone (Naphthazarin)	*298*	3·52	297	2·60
2 : 5 : 8-Trihydroxy-1 : 4-naphthaquinone (Naphthapurpurin)	*289*	3·92	286	3·74
Hydroxyjuglone	*286*	4·12		
2 : 3-Dihydroxy-1 : 4-naphthaquinone (*iso*Naphthazarin)	*282*	4·05	283	3·74
Naphthazarin	*284*	3·84		
2-Hydroxy-1 : 4-naphthaquinone.......................................	*276*	4·20	275	3·90
5 : 8-Dihydroxy-2-methyl-1 : 4-naphthaquinone (2-Methylnaphthazarin)	275	3·98		
*iso*Naphthazarin...	270	4·12	273	3·90
Naphthazarin	270	3·92		
Naphthapurpurin	268	4·20		
2 : 3-Diacetoxy-1 : 4-naphthaquinone (*iso*Naphthazarin diacetate)	268	4·15	265	3·78
2-Acetoxy-1 : 4-naphthaquinone	*262*	4·14		
5-Hydroxy-1 : 4-naphthaquinone (Juglone)	*262*	4·00		
5 : 8-Diacetoxy-2-methyl-1 : 4-naphthaquinone (2-Methylnaphthazarin diacetate)	*256*	4·09		
5 : 8-Diacetoxy-1 : 4-naphthaquinone (Naphthazarin diacetate) ...	*256*	4·05		
5-Acetoxy-1 : 4-naphthaquinone (Juglone acetate)	255	4·05		
Naphthazarin	*254*	3·82	256	3·70
Naphthapurpurin	*252*	4·36		
1 : 4-Naphthaquinone	*256*	4·13		
2-Methyl-1 : 4-naphthaquinone	*259*	4·23		
3 : 5 : 8-Trihydroxy-2-methyl-1 : 4-naphthaquinone (Hydroxydroserone)	*298*	3·92	297	2·60
Hydroxydroserone	*255*	3·95	256	3·70
3 : 5 : 8-Triacetoxy-2-methyl-1 : 4-naphthaquinone (Hydroxydroserone triacetate)	*265*	4·06	265	3·78

in the naphthaquinones, it would seem more satisfactory to attribute the maxima recorded above to similar vibrations rather than to postulate a naphthenoid structure.

TABLE II.

λ 240—250 mμ.

Substance.	λ_{max}.	log ϵ.	Substance.	λ_{max}.	log ϵ.
Methylnaphthazarin diacetate	240	4·17	Naphthazarin...........................	247	·3·73
Hydroxyjuglone	240	3·96	2-Methyl-1 : 4-naphthaquinone ...	248	4·27
2-Hydroxy-1 : 4-naphthaquinone...	244	4·20	2-Acetoxy-1 : 4-naphthaquinone...	248	4·26
Naphthazarin diacetate...............	244	4·16	Juglone	249	4·12
Juglone acetate	245	4·16	2-Hydroxy-1 : 4-naphthaquinone	249	4·24
isoNaphthazarin diacetate	246	4·21	Hydroxydroserone	239	4·27
1 : 4-Naphthaquinone	246	4·28	Hydroxydroserone triacetate	241	4·09

Some other characteristics shown by the curves are set down in Table III. An absorption in the region λ 330 mμ occurs in all the quinones and their acetates, except those containing hydroxyl groups in the *peri*-positions. In the latter case the band is either missing or modified to an inflexion, but in the acetates of such compounds a definite band is present; and it is significant that when two *peri*-acetoxyl groups are found in the compound the maximum is at λ 351 mμ.

It is probable that the absorption in this region is due to the chromophore C=C—C=C, and Morton, Hassan, and Calloway (*loc. cit.*) are of the opinion that in a chromophore of this type the absorbing electron is in the C=C linkage when the molecular extinction coefficients are of the order 10^3—10^5 as is the case in the naphthaquinones. The log ϵ values are remarkably constant for the substances examined, apart from the inflexions already mentioned in the quinones containing two *peri*-hydroxyl groups.

TABLE III.

Substance.	λ_{max}.	log ϵ.			
1 : 4-Naphthaquinone	334	(3·44)			
2-Methyl-1 : 4-naphthaquinone	333	(3·37)			
2-Hydroxy-1 : 4-naphthaquinone..........................	331	(3·45)			
2-Acetoxy-1 : 4-naphthaquinone	333	(3·41)			
Naphthazarin	338	(2·95),	450 (3·50),	485 (3·75),	513 (3·85) *
Naphthazarin diacetate....................................	352	(3·42)			
Methylnaphthazarin	331	(2·72),	454 (3·60),	481 (3·75),	510 (3·81) *
Methylnaphthazarin diacetate	352	(3·38)			
Juglone	339	(3·18)			
Juglone acetate	338	(3·41)			
isoNaphthazarin...	335	(3·31)			
isoNaphthazarin diacetate	338	(3·42)			
Hydroxyjuglone	—	—			
Naphthapurpurin	—	—	440 (3·71),	485 (3·85),	523 (3·70) †
Hydroxydroserone	—	—	—	—	488 (3·83), 518 (3·71) †
Hydroxydroserone triacetate	351	(3·43)			

Also inflexions in the region λ 410—440 mμ (1·78—2·15) in the case of simple 1 : 4-naphthaquinones and their acetates; but these are absent in derivatives with two substituents (acetoxyl or methyl) in the quinone ring.

* Two *peri*-OH-groups.   † Two *peri*-OH-groups and OH in the quinone ring.

4-*Methoxy*-1 : 2-*naphthaquinone.*—The curves for 1 : 2-naphthaquinone recorded by Goldschmidt and Graef (*loc. cit.*) show maxima in alcoholic solution in close agreement with those now found in the case of 4-methoxy-1 : 2-naphthaquinone :

| 1 : 2-Naphthaquinone.		4-Methoxy-1 : 2-naphthaquinone.	
λ_{max}.	log ϵ.	λ_{max}.	log ϵ.
500	2·00	490	2·20
400	3·40	403	3·29
340	3·40	339	3·26
—	—	273	3·78
—	—	254	4·01
250	4·35	250	4·07

The definite maximum in the region λ 400 mμ, and the inflexion in the region 490—500 mμ, are without parallel in the absorption characteristic of the 1 : 4-naphthaquinone

type, and may reasonably be applied as a criterion to distinguish between the 1 : 2- and the 1 : 4-structure. Qualitative examination of the absorption of 7-hydroxy-1 : 4-naphthaquinone showed that, as in the case of the 1 : 4-compounds, the introduction of the hydroxyl group modifies the characteristic curves of the simple substances : a sample of the acetate was not available, but it is to be expected that further work will show that acetylation will in such cases also cause a reversion to the standard type.

Hydroxydroserone.—A comparison of the curves of simple 1 : 4-naphthaquinones and the acetates of hydroxy-1 : 4-naphthaquinones shows that hydroxydroserone triacetate conforms closely to the general type : and a 1 : 4-structure may therefore be inferred. It is also evident that hydroxydroserone itself more closely resembles those derivatives such as naphthazarin, methylnaphthazarin, and naphthapurpurin in which two hydroxyl groups are *peri* to the quinone oxygen atoms. Thus, in the region λ 330—350 mμ, the values for the acetates of naphthazarin, methylnaphthazarin, and hydroxydroserone are practically identical (a sample of the acetate of naphthapurpurin was not available) and are considerably higher than those for the other acetates examined. In the region λ 240—250 mμ, 1 : 4-naphthaquinone, 2-methyl-1 : 4-naphthaquinone, 2-acetoxy-1 : 4-naphthaquinone, and *iso*naphthazarin diacetate have almost the same $\lambda_{max.}$ (246—248 mμ), whilst the value for juglone acetate is somewhat lower (245 mμ), and those for the acetates of naphthazarin, methylnaphthazarin, and hydroxydroserone are still lower (240—244 mμ). The log ε values for the first four substances are also higher. In the region λ 250—300 mμ, the log ε values for the same four compounds lie close together, and are lower than those of the other substances under discussion. These facts indicate that hydroxydroserone contains at least one, but more probably two, hydroxyl groups in *peri*-positions.

Inspection of the curves also shows that substitution in the quinone ring expresses itself in the region λ 240—280 mμ : in this region hydroxydroserone triacetate shows points of similarity to *iso*naphthazarin diacetate, and it may thus be inferred that the quinone ring is fully substituted : and the absence of inflexions at λ 410—440 mμ in these two cases is a further point of agreement. Since the presence of two *peri*-hydroxyl groups has already been suggested, the introduction of the methyl group and the remaining hydroxyl into the quinone ring leads to the structure (III) for hydroxydroserone. This has been confirmed by a study of the reactivity of the compound (see following paper).

(III)

Colour Reactions of Naphthaquinones (with A. B. BECK).—Ionescu (*Bull. Soc. chim.,* 1927, **41**, 1094) showed that certain quinones react with substances containing an active methylene group, and formulated the change as a two-stage reaction involving the methylene group :
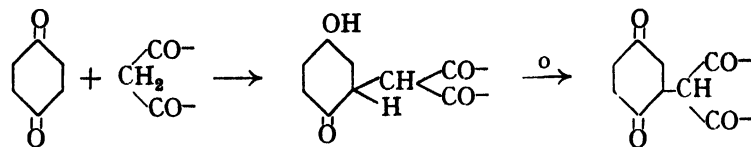
Later, Kesting (*Z. angew. Chem.,* 1928, **41**, 358, 745) described the colour reactions of naphthaquinones and malononitrile, and in a further paper (*Ber.,* 1929, **62**, 1422) discussed those of quinones and compounds of the structure −(E):C·CH₂·C:(E)−, where E is a multivalent element. *p*-Benzoquinone and 1 : 2- and 1 : 4-naphthaquinones gave colours with such substances as malononitrile, ethyl cyanoacetate, cyanoacetamide, acetyl- and benzoyl-acetone, and ethyl aceto- and benzoyl-acetate. In cases where the p_H of the quinone was less than that of the solvent, colours were obtained without the further addition of alkali, but otherwise the addition of ammonia or other base was essential. We have examined the series of naphthaquinones now available, and find that on treatment in alcoholic-solution with ethyl cyanoacetate and ammonia colorations are given by juglone, naphthazarin and methylnaphthazarin : the acetates of these compounds gave similar colorations, but the rate of development was considerably reduced. The following 1 : 4-naphthaquinones and such of their acetates as were available gave no colorations apart

from the colour of their ammonium salts : 2-hydroxy-, 2 : 3-dihydroxy-, 2 : 5-dihydroxy-, 2 : 8-trihydroxy-. For such hydroxy-quinones as gave coloured ammonium salts, a Hellige colorimeter was used throughout to detect intensity changes, if any, on the addition of the cyanoacetate.

From the results, it appears that introduction of even one hydroxy group in the quinone nucleus is sufficient to inhibit colour production, although the hydrogen atom required by the formulations of Ionescu and Kesting is still available. Since neither hydroxy-droserone nor its acetate gave any positive test, this behaviour may be taken as additional evidence that a hydroxyl group is present in the quinone ring.

The behaviour of a further series of $-(E){:}C{\cdot}CH_2{\cdot}C{:}(E)-$ compounds with 1 : 4-naphtha-quinone was studied in order to supplement the results of previous workers. Colorations were obtained in all cases, except with tribenzoylmethane. In view of the fact that Craven (J., 1931, 1606) is examining the constitutions of such derivatives, we did not extend work in this direction.

Brissemoret and Coombes (*J. Pharm. Chim.*, 1907, **25**, 53) found that nickel acetate formed co-ordination compounds with hydroxynaphthaquinones, the reaction being indicated by the formation of blue, or violet-blue, colorations when dilute solutions of the reagents were mixed. Examination of the hydroxynaphthaquinones now available shows that colours other than those stated are produced in some cases, and since *iso*naphthazarin gives an intense blue colour, the reaction is not inhibited by two hydroxyl groups in the quinone ring.

EXPERIMENTAL.

2-Hydroxy-1 : 4-naphthaquinone prepared by Fieser's method (*loc. cit.*) had m. p. 189° (decomp.). Methylation by diazomethane gave the 2-methoxy-derivative, which after crystall-isation from water had m. p. 183·5°. The 2-acetoxy-derivative was prepared by direct acetyl-ation with acetic anhydride and zinc chloride, and had m. p. 131°.

2-Methyl-1 : 4-naphthaquinone was prepared by adding 2-methylnaphthalene in glacial acetic acid to a cold solution of chromic acid in 80% acetic acid (Madinaveitia and de Buruaga, *Anal. Soc. Fís. Quím.*, 1929, **27**, 647); yellow needles from glacial acetic acid, m. p. 106°.

4-Methoxy-1 : 2-naphthaquinone was prepared by the alkylation of the silver salt of 2-hydroxy-1 : 4-naphthaquinone (Fieser, *loc. cit.*); orange-red needles from benzene, m. p. 190°.

5-Hydroxy-1 : 4-naphthaquinone (juglone), prepared from 1 : 5-dihydroxynaphthalene by Willstätter and Wheeler's method (*Ber.*, 1914, **47**, 2796), after recrystallisation from light petroleum had m. p. 150—151° in a bath preheated to 140°. The acetate (Bernthsen and Semper, *Ber.*, 1885, **18**, 206), pale yellow needles from alcohol, had m. p. 154—154·5°.

2 : 5-Dihydroxy-1 : 4-naphthaquinone (oxyjuglone), prepared by Mylius's method (*Ber.*, 1885, **18**, 469) by the oxidation of hydrojuglone (Willstätter and Wheeler, *loc. cit.*), had m. p. 210° (decomp.).

2 : 3-Dihydroxy-1 : 4-naphthaquinone (*iso*naphthazarin) was an I.-G. product which was repeatedly recrystallised from glacial acetic acid. The diacetyl derivative, prepared by the continued action of acetyl chloride (Wheeler and Edwards, *J. Amer. Chem. Soc.*, 1917, **39**, 2465), after recrystallisation from glacial acetic acid had m. p. 191°. We found methods involving the use of acetic anhydride unsatisfactory (Zincke and Schmidt, *Annalen*, 1895, **286**, 36; Thiele and Winther, *ibid.*, 1900, **311**, 348), the product repeatedly recrystallised from alcohol having m. p. 134°.

2 : 5 : 8-Trihydroxy-1 : 4-naphthaquinone (naphthapurpurin) is difficult to prepare in the pure state (Fieser, *J. Amer. Chem. Soc.*, 1928, **50**, 460; Thiele and Winther, *loc. cit.*; Dimroth and Roos, *Annalen*, 1927, **456**, 191). A pure sample, in poor yield, was obtained by condensing maleic anhydride (2 g.) with 1 : 2 : 4-trihydroxybenzene (1 g.), the mixture being added to a melt of aluminium chloride (20 g.) and sodium chloride (4 g.) at 180°; the temperature rose to about 200° and was maintained there for some 5 mins. The melt was then heated to 220°, and the pasty mass removed from the crucible before solidification, dissolved in water, and after the addition of an equal volume of concentrated hydrochloric acid the solution was heated till the colour of the aluminium chloride complex changed to dull-red. After cooling in ice, the solid was filtered off, and the filtrate extracted with chloroform. The dried solid was also repeatedly extracted with chloroform, and the combined extracts shaken with sodium hydroxide solution. The solid precipitated from the alkaline extract on the addition of concentrated hydrochloric acid was dried and extracted (Soxhlet) with light petroleum for several days;

a small amount of very pure crystalline material then collected in the flask. Sufficient was not available to form the triacetate, which is not described in the literature.

Methylnaphthazarin (5 : 8-dihydroxy-2-methyl-1 : 4-naphthaquinone) was prepared (*a*) by condensing maleic anhydride with toluquinol and (*b*) by condensing citraconic anhydride with quinol. The two products were identical. The procedure followed closely that described in the preceding case, but the product was crystallised from alcohol. In appearance, it closely resembles naphthazarin, having the same brilliant green sheen; m. p. 173° (Found : C, 64·7; H, 4·0. $C_{11}H_8O_4$ requires C, 64·7; H, 3·8%).

Methylnaphthazarin diacetate is best prepared by refluxing methylnaphthazarin with excess acetyl chloride for several days, or until the red colour disappears. After addition of glacial acetic acid, the acetyl chloride is distilled off and the diacetate crystallises on cooling. After two crystallisations from benzene–light petroleum, it has m. p. 168° (Found : C, 62·7; H, 4·4. $C_{15}H_{12}O_6$ requires C, 62·5; H, 4·2%).

Derivatives of Naphthalene-1 : 5-*disulphonyl Chloride.*—In the preparation of naphthalene-1 : 5-disulphonic acid required in the synthesis of juglone (Bernthsen and Semper, *Ber.*, 1887, 20, 924), a copious white precipitate was obtained when the reaction mixture of naphthalene and chlorosulphonic acid was poured into water. It was identified as naphthalene-1 : 5-disulphonyl chloride, white prisms, m. p. 179°, from ether, benzene, acetone, or carbon tetrachloride (cf. 183°; Armstrong, *Ber.*, 1882, 15, 205). Naphthalene-1 : 5-disulphonamide was obtained on treating the dichloride with a little alcohol and large excess of aqueous ammonia, boiling, and filtering. Unchanged dichloride was extracted from the residue by acetone. The diamide was slightly soluble in aniline, but practically insoluble in other organic solvents and had no sharp m. p. Naphthalene-1 : 5-bisdimethylsulphonamide was prepared (*a*) by methylating the amide with methyl sulphate and alkali and (*b*) by warming the dichloride with sodium hydroxide and dimethylamine hydrochloride. After recrystallisation from acetone, both samples had m. p. 241—242°. Phenyl naphthalene-1 : 5-disulphonate was obtained on the addition of the dichloride in acetone to sodium phenoxide. On addition of water after evaporation of part of the acetone a precipitate of the crude ester was thrown down, which separated as faintly pink prisms, m. p. 173—174° from acetone.

Naphthalene-1 : 5-disulphinic acid, sparingly soluble in water, m. p. 162—163°, was obtained on boiling the dichloride with aqueous sodium sulphite. The disulphinic acid crystallised on cooling the hot filtrate acidified with sulphuric acid. It responds to Smiles's test (concentrated sulphuric acid and anisole, blue colour) for aromatic sulphinic acids.

Colorations with $-(E)\!:\!C\!\cdot\!CH_2\!\cdot\!C\!:\!(E)-$ *Compounds.*—In the cases tabulated below 1 : 4-naphthaquinone was taken as a standard test quinone, and gave the range of colours recorded (Mulliken's charts) when treated with alcoholic solutions of the reagents listed. The rate of colour change varied from case to case. Tests with juglone and naphthazarin gave a similar range of colours, and in all cases 0·1 g. of the reagent was added to 5 ml. of an $M/1000$-alcoholic solution of the quinone, and 3 ml. of a mixture of equal parts of alcohol and ammonia (*d*, 0·880) added.

Reagent.	Colour change ($\longrightarrow$).		
Ethyl malonate	Blue.	Violet.	Brn.†
*iso*Amyl malonate	Blue.	Bkn Violet.	Brn.
Ethyl ethylmalonate	Blue.	Bkn Violet.	Brn.
Ethyl diethylmalonate	Pale Bkn Blue.*		Brn.
Ethyl cyanoacetate	Violet-blue.	Green.	Brn.
Ethyl acetoacetate	Blue-violet.	Violet-red.	Brn.
Acetylacetone	Red-violet.	Violet-red.	
Benzoylacetone	Blue-violet.	Violet.	Violet-red.
Dibenzoylmethane	Blue-violet.	Violet.	
Tribenzoylmethane	Yellow (very faint).		

* Colour due to traces of ethyl ethylmalonate.

† Brn denotes an indefinite range between Bkn Red and Bkn Yellow.

Colorations with Nickel Acetate.

Reagent.	Colour.	Reagent.	Colour.
2-Hydroxy-1 : 4-naphthaquinone	Yellow-orange	Naphthazarin	Blue
Juglone	Violet-red	*iso*Naphthazarin	,,
Lapachol	,,	Hydroxyjuglone	Red
Hydroxyhydrolapachol	,,	Naphthapurpurin	Red-violet
Dihydroxyhydrolapachol	,,		

71. *The Colouring Matters of* Drosera Whittakeri. *Part II.*

By A. Killen Macbeth and F. L. Winzor.

The suggestion (preceding paper) that hydroxydroserone is 3 : 5 : 8-trihydroxy-2-methyl-1 : 4-naphthaquinone is supported by the results obtained with several reagents which detect the positions of hydroxyl groups in quinonoid compounds.

Boroacetic anhydride, which was introduced as a reagent for *peri*-hydroxyl groups by Dimroth *et al.* (*Ber.*, 1921, **54**, 3020; *Annalen*, 1925, **446**, 97), gives a *diboroacetate* with methylnaphthazarin, but only acetylates 2-hydroxy-1 : 4-naphthaquinone. Since hydroxydroserone yields a *diboroacetate*, the presence of two *peri*-hydroxyl groups may be deduced; the third hydroxyl group is acetylated. Droserone, on the other hand, yields a *monoboroacetate*, a fact which suggests that it is probably 3 : 5 (or 3 : 8)-dihydroxy-2-methyl-1 : 4-naphthaquinone. It is difficult to remove all traces of hydroxydroserone from the less oxygenated compound, but Rennie (*J.*, 1893, **63**, 1083) found that partial oxidation of droserone gave a yellow substance, m. p. 178° : since yellow needles of the same m. p. are recovered on decomposition of the boroacetate, it appears that the oxidation referred to merely resulted in the removal of traces of hydroxydroserone present, and that purification may also be effected through the boroacetate.

The reaction of stannic chloride and hydroxyanthraquinones (Pfeiffer *et al.*, *Annalen*, 1913, **398**, 137) led to the conclusion that a $SnCl_3$-complex is formed when one *peri*-hydroxyl group is present, whereas with two such groups in the same nucleus a $SnCl_2$-complex is produced, and in no case is a complex formed with a hydroxyl group in another position. On the other hand, Pfeiffer showed that hydroxyl groups in positions other than the *peri*-positions are sufficiently acidic to form pyridine salts. These reactions also held for such hydroxynaphthaquinones as were examined (Pfeiffer, Oberlin, and Segall, *Ber.*, 1927, **60**, 111; Dimroth and Roos, *Annalen*, 1927, **456**, 177). 2-Hydroxy-1 : 4-naphthaquinone, however, combines with one molecule of pyridine and also forms a $SnCl_3$-complex; from which it appears that a 2-hydroxyl group reacts in a similar way to a *peri*-hydroxyl, and stannic chloride is not a specific reagent for the latter. *iso*Naphthazarin, like naphthazarin, forms a $SnCl_2$-complex and, like hystazarin, forms a monopyridine salt. Droserone and hydroxydroserone both give *monopyridine* salts, and so contain at least one hydroxyl in a position other than the *peri*-position : the stannichlorides in these cases were not isolated in a state sufficiently pure to warrant analysis.

Diazomethane combines additively with 1 : 4-benzo- and naphtha-quinones (Pechmann and Seel, *Ber.*, 1899, **32**, 2292; Fieser and Peters, *J. Amer. Chem. Soc.*, 1931, **53**, 4080), but 2-hydroxy- and 2 : 3-dihydroxy-1 : 4-naphthaquinones are methylated, and we have never found addition to occur in these cases even in presence of a large excess of the reagent. Since an alkyl substituent in the quinone ring also appears to inhibit the formation of an additive compound, 2-methyl-1 : 4-naphthaquinone giving negative results, it seemed that the reaction with diazomethane might furnish evidence of the nature of the substitution in hydroxydroserone. This was vigorous and analysis of the product showed that one molecule of diazomethane condensed with a molecule of the quinone, with simultaneous methylation of one hydroxyl group. Work on the reaction of diazomethane and quinones is proceeding, but the present results appear to imply that in hydroxydroserone there are two adjacent unsubstituted positions in the quinone ring. The results therefore point to formula (I) for the compound.
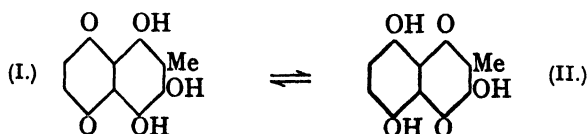
Fieser's deduction of the structure of naphthapurpurin, based on a study of the reduction potentials of hydroxynaphthaquinones (*J. Amer. Chem. Soc.*, 1928, **50**, 439), indicates that the form containing three hydroxyl groups in the same nucleus is unstable, and can

exist only in extremely small amount in the equilibrium mixture of the two forms. In accordance with this view formula (II) would better represent the structure of hydroxydroserone. This formula is also in accord with the colour reactions and absorption spectra (preceding paper), and to account for the reaction with diazomethane it is only necessary to assume tautomerisation to the alternative structure in the presence of a suitable reagent. That tautomerisation of this type readily occurs is seen in the case of methylnaphthazarin, which is synthesised either by the condensation of (*a*) maleic anhydride and toluquinol or (*b*) citraconic anhydride and quinol (this vol., p. 333) :
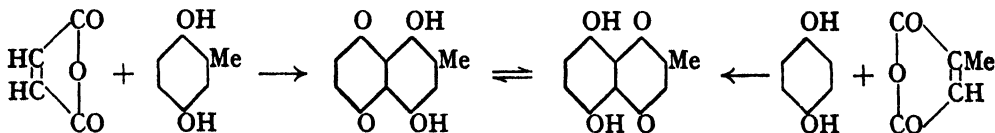
<div align="center">EXPERIMENTAL.</div>

Boroacetates.—The boroacetates were formed by warming the colouring matter with acetic anhydride in the presence of boric acid. If the boroacetate did not separate on cooling, the excess of anhydride was removed under reduced pressure. In the analysis of the compounds the following estimations were carried out : (*a*) the acetyl value of the product, which was determined by a slight modification of Perkin's method, the ethyl acetate being distilled into a known volume of standard alcoholic potassium hydroxide and the alkali consumption measured by the addition of excess of hydrochloric acid, the surplus being found (after boiling to expel carbon dioxide) by titration with baryta in the presence of neutral-red; (*b*) the percentage residue after hydrolysis of the boroacetate by cold water; (*c*) the acetyl value of this residue; (*d*) the total acidity of the filtrate from (*b*) by titration with baryta and phenolphthalein, after the addition of mannitol; (*e*) the percentage of boron in the boroacetate, which is calculated from the boric acid value $d-(a-c)$.

Methylnaphthazarin diboroacetate. Boric acid (0·4 g.) in acetic anhydride (10 c.c.) was added to a solution of the quinone (1 g.) in acetic anhydride (10 c.c.) at 50—60°. The *boroacetate* crystallised in reddish-violet plates on cooling, and was washed with acetic anhydride and with ether (dried over sodium) [Found : (*a*) 36·6; (*b*) 44·0; (*c*) nil; (*d*) 0·2451 g. required 7·5 c.c. of baryta (0·429N), calc., 7·45 c.c.; (*e*) 5·0. $C_{11}H_6O_4B_2(OAc)_4$ requires (*a*) 37·4; (*b*) 44·3; (*e*) 4·8%].

Hydroxydroserone diboroacetate. Finely powdered hydroxydroserone (1 g.) was slowly added to warm acetic anhydride (50 c.c. at 50—60°) containing boric acid (0·6 g.). The solution was filtered hot through fritted glass and concentrated under reduced pressure to 15 c.c.; on standing in a closed flask in the ice-chest, the *diboroacetate* separated as a red crystalline powder which was treated as in the preceding case [Found : (*a*) 41·1; (*b*) 50·8; (*d*) 0·2050 g. required 5·0 c.c. of baryta (0·459N), calc., 5·17 c.c.; (*e*) 4·2. $C_{11}H_5O_4B_2(OAc)_5$ requires (*a*) 41·5; (*b*) 50·6; (*e*) 4·2%. Found : (*c*) 15·6. Calc. for $C_{11}H_7O_4(OAc)$: 16·4%].

Hydroxydroserone 3-monoacetate obtained on hydrolysis of the boroacetate by cold water had m. p. 151—156° when thrice recrystallised from benzene. When heated with acetic anhydride and a little zinc chloride, it yielded the triacetate, m. p. 156°, identical with that prepared directly from hydroxydroserone.

Droserone boroacetate. Only a small amount of material was available, but analysis of the product isolated in the usual way indicated that a *monoboroacetate* mainly is formed, but the second hydroxyl group undergoes partial acetylation [Found : (*a*) 27·2; (*b*) 63·1; (*c*) traces; (*d*) 0·1025 g. required 2·4 c.c. of baryta (0·382N), calc., 2·42 c.c.; (*e*) 3·1. $C_{11}H_7O_4B(OAc)_2$ requires (*a*) 25·8; (*b*) 61·5; (*e*) 3·3%].

The residue after hydrolysis of the boroacetate by cold water melted at *ca.* 170°, but after warming with sodium hydroxide, reprecipitation by acid, and crystallisation from alcohol was isolated as yellow needles of pure droserone, m. p. 178°.

2-Hydroxy-1 : 4-naphthaquinone gave no boroacetate even on concentration of the reaction mixture. The solid precipitated by water was 2-acetoxy-1 : 4-naphthaquinone, m. p. 131° after crystallisation from alcohol. Had a boroacetate been formed, the hydroxyquinone itself, m. p. 190°, would have been recovered.

Stannichloride Compounds and Pyridine Salts.—In the preparation of the stannichloride compounds, solutions of the hydroxyquinone and stannic chloride in hot anhydrous benzene were

mixed and heated under reflux for several hours. The tin complex which separated was quickly filtered off, washed free from hydrochloric acid and excess of stannic chloride with dry benzene, and stored in a desiccator over phosphoric oxide. The stannichlorides isolated contain a molecule of benzene, and are contaminated with traces of adhering benzene which it is difficult to remove completely : this, although affecting the percentage composition, does not alter the tin–chlorine ratio. The tin complex on hydrolysis on the water-bath with a mixture of water (25 c.c.) and saturated ammonium nitrate solution (25 c.c.) gives a precipitate, which is ignited and weighed as SnO_2. Chloride in the filtrate, acidified with nitric acid, is estimated gravimetrically as silver chloride.

*2-Hydroxy-*1 : 4-*naphthaquinone.* To the quinone (0·4 g.) dissolved in anhydrous benzene (50 c.c.), stannic chloride (0·5 c.c.) in the same solvent was added, and the mixture refluxed on the water-bath for 2 days. The yellow-brown precipitate was analysed directly after preparation (Found : Sn, 22·5, 22·6; Cl, 19·9, 21·1; Sn : Cl = I : 2·95, 2·97. $C_{10}H_5O_3SnCl_3 + C_6H_6$ requires Sn, 25·0; Cl, 22·25%). The *pyridine* salt crystallised as orange-red needles from a solution of the quinone in hot pyridine, and all the pyridine was lost on heating at 110° (Found : pyridine, 31·1. $C_{10}H_6O_3Py$ requires Py, 31·2%).

2 : 3-*Dihydroxy-*1 : 4-*naphthaquinone.* The *tin complex* separated as a green powder when a solution of the quinone (0·4 g.) in anhydrous benzene (50 c.c.) containing stannic chloride (1 c.c.) was refluxed for 6 hours and cooled (Found : Sn, 23·6, 23·9; Cl, 14·2, 14·3; Sn : Cl = 1 : 1·98, 2·03. $C_{10}H_4O_4SnCl_2 + C_6H_6$ requires Sn, 26·1; Cl, 15·6%). The *pyridine* salt, which is very soluble, was obtained by the addition of excess of light petroleum to a solution of the quinone in pyridine. After filtration and quick washing with light petroleum, the salt was pressed between filter-papers and stored in a desiccator over phosphoric oxide for 2 hours (Found : Py, completely removed at 110°, 29·8. $C_{10}H_6O_4Py$ requires Py, 29·4%).

Hydroxydroserone. The stannichloride was not isolated in a pure state, but the *pyridine* salt separated as bright red needles when a hot pyridine solution of the quinone was cooled (Found : Py lost at 110°, 26·4. $C_{11}H_8O_5Py$ requires Py, 26·4%).

Droserone gave a *pyridine* salt which separated as needles of a somewhat more orange tint than the preceding compound (Found : Py, 27·7. $C_{11}H_8O_4Py$ requires Py, 27·9%).

Action of Diazomethane.—(I) On addition of an ethereal solution of diazomethane to 2-hydroxy-1 : 4-naphthaquinone suspended in ether, the quinone dissolved, but the methyl ether soon separated as small, pale yellow crystals, m. p. 183° after recrystallisation from alcohol, identical with 2-methoxy-1 : 4-naphthaquinone prepared by the action of acid methyl alcohol on the quinone (Fieser, *J. Amer. Chem. Soc.*, 1926, **48**, 2932).

(2) *iso*Naphthazarin dimethyl ether, yellow needles, m. p. 115°, was obtained in a similar way (compare Fieser, *ibid.*, 1928, **50**, 461).

(3) There was a vigorous reaction on the addition of an ethereal solution of diazomethane to a suspension of hydroxydroserone in dry ether, and after previous solution a product was precipitated in brown needles, m. p. 189° after crystallisation from alcohol and from glacial acetic acid [Found : N, 10·9; OMe, 10·9. $C_{13}H_7O_4N_2(OMe)$ requires N, 10·2; OMe, 11·3%].

72. *The Colouring Matters of* Drosera Whittakeri. *Part III. The Synthesis of Hydroxydroserone.*

By F. L. Winzor.

In the two preceding papers it has been shown that droserone is probably 3 : 5 (or 3 : 8)-dihydroxy-2-methyl-1 : 4-naphthaquinone, and hydroxydroserone the 3 : 5 : 8-trihydroxy-2-methyl compound. The methods involved, however, do not provide absolute proof, and since oxalic and acetic acids were the only isolable products on oxidation, and methylnaphthalene was not obtained in the degradation experiments carried out, it is desirable to establish the structures of the colouring matters by synthesis : this has now been achieved in the case of hydroxydroserone. The condensation of maleic anhydride with a suitable phenolic substance—successfully applied by Zahn and Ochwat (*Annalen*, 1928, **462**, 51) in the synthesis of naphthazarin, and by Macbeth, Price, and Winzor (this vol., p. 333)—appeared to be the most promising line of attack. The obvious starting material,

2 : 3 : 6-trihydroxytoluene, is not available, since toluquinone on treatment with acetic anhydride and sulphuric acid yields 2 : 4 : 5-triacetoxytoluene. 3 : 6-Dihydroxy-2-methoxytoluene (IV) is, however, available by the following series of reactions, and when condensed with maleic anhydride gives a product identical with hydroxydroserone.

(I.) (II.) (III.) (IV.)

(V) (VI)
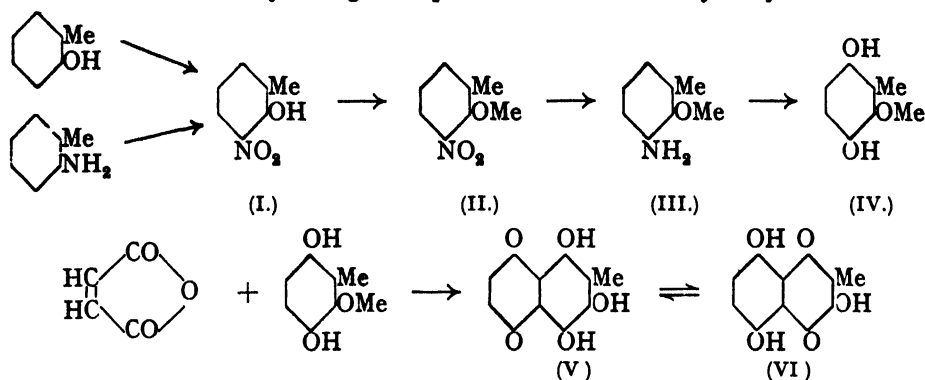
The structure is further supported by the synthesis of the isomeric quinone with the methyl group in the other nucleus, 3 : 5 : 8-trihydroxy-6 (or 7)-methyl-1 : 4-naphtha-quinone (VII, VIII), which is prepared by the condensation of citraconic anhydride and 1 : 2 : 4-trihydroxybenzene. This product resembles hydroxydroserone in its colour reactions, but differs from it markedly in that it is exceedingly difficult to crystallise. The experimental product is possibly a mixture of the 6- and the 7-methyl compound, and on account of the doubt as to its homogeneity its derivatives have not yet been investigated.

(VII.) or (VIII)
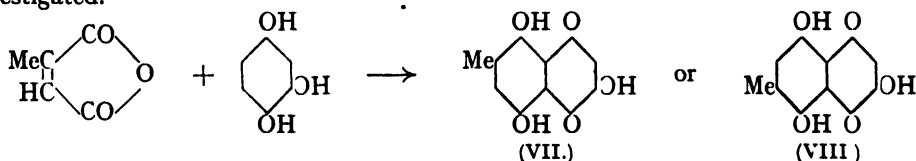
Of the tautomeric forms (V, VI) of hydroxydroserone, the second is regarded as the more stable in accordance with the evidence submitted in the previous papers. Hydroxy-droserone thus falls into line with the structures of other well-known, naturally occurring hydroxynaphthaquinones such as lapachol (IX; Hooker, J., 1896, **69**, 1355; Fieser, *J. Amer. Chem. Soc.*, 1927, **49**, 857), lomatiol (X; Hooker, *loc. cit.*, p. 1381), and shikonin (XI; Majima and Kuroda, *Acta Phytochim.*, 1922, **1**, 43).

(IX) (X) (XI)
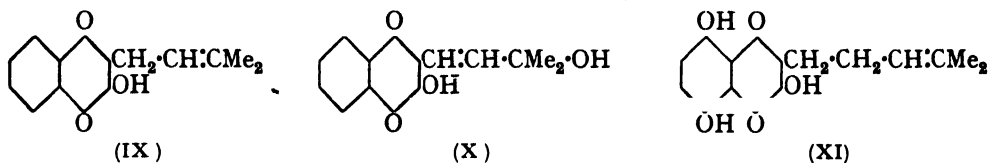
Shikonin presents a close parallel in its substituents to hydroxydroserone, and the formula proposed for the stable form of the compound is further supported by the fact that on heating shikonin gives a sublimate of 5-methylquinizarin.

EXPERIMENTAL.

3-*Nitro-o-cresol* (I).—*o*-Cresol (100 g.), dissolved in benzene (200 g.), was nitrated at 20° with nitric acid (530 g., *d* 1·21) (Schultz, *Ber.*, 1907, **40**, 4319); after the nitration additional benzene was added to assist in breaking down the emulsion. The benzene solution having been washed free from nitric acid, the mixture was steam distilled, giving almost pure 3-nitro-*o*-cresol, but if the distillation was prolonged some dinitro-compound also passed over. Repetition of the steam distillation gave the 3-nitro-derivative (20 g.) in a pure state; m. p. 67°.

z

An alternative method makes use of the nitrating action of excess of nitrous acid on diazonium compounds (Denninger, *J. pr. Chem.*, 1889, **40**, 299; Khotinsky and Jacopson-Jacopmann, *Ber.*, 1909, **42**, 3099). The best yield was obtained from *o*-toluidine (23 g.) dissolved in concentrated sulphuric acid (40 c.c.) and water (160 c.c.). The solution was cooled to 15°, and sodium nitrite (60 g.) in water (200 c.c.) added, gradually at first and then rapidly, the temperature being allowed to rise. The reaction mixture was poured at once into an excess of sulphuric acid (50%) contained in a large dish heated on a water-bath. After the vigorous evolution of gas had subsided, the mixture was steam distilled. Yield, 9·3 g. of pure product.

3-Nitro-2-methoxytoluene (II) and 2-methoxy-*m*-toluidine (III) were prepared by the methods of Shah, Bhatt, and Kanga (J., 1933, 1376). We found that these compounds boiled at 250° and 225° respectively, instead of 225° and 253° recorded by the above workers, who have evidently transposed the boiling points.

3 : 6-Dihydroxy-2-methoxytoluene (IV) was prepared by the method of Majima and Okazaki (*Ber.*, 1916, **49**, 1490). 2-Methoxy-*m*-toluidine (8 g.) in concentrated sulphuric acid (50 c.c.) and water (160 c.c.) was gradually treated with sodium dichromate (8 g.) in water (40 c.c.) with vigorous shaking at 3—5°. After 12 hours 16 g. of dichromate in water were added within the same temperature limits, and after several hours the mixture was repeatedly extracted with ether. After removal of the solvent the residue was steam distilled, and the distillate was saturated with sulphur dioxide, kept over-night, and repeatedly extracted with ether. Evaporation of the dried extract and recrystallisation of the residue from benzene gave (IV) as white needles (1 g.), m. p. 117—118°.

3 : 5 : 8-*Trihydroxy-2-methyl-1 : 4-naphthaquinone* (*Hydroxydroserone*) (V, VI).—The preceding quinol (1 g), finely ground with an excess of maleic anhydride (2 g.), was added to a melt of anhydrous aluminium chloride (20 g.) and sodium chloride (4 g.) at 180°. The temperature rose spontaneously to 200° and was maintained at that point for about 5 minutes and then raised to 220°. The paste-like melt was dissolved in water and, after the addition of an equal volume of concentrated hydrochloric acid, heated till the purple-red colour had changed to dull red. The solid separating on cooling in ice was filtered off, and the filtrate extracted with chloroform. The solid after drying in a vacuum was boiled several times with chloroform until the extract was coloured only faintly yellow. The combined extracts were shaken with aqueous sodium hydroxide, which, when separated and acidified with hydrochloric acid, gave a bright scarlet, flocculent precipitate of the colouring matter. After one crystallisation from glacial acetic acid the product (0·5 g.) had m. p. 192—193°, alone or mixed with hydroxydroserone obtained from natural sources (Found : C, 59·8; H, 3·3. Calc. for $C_{11}H_8O_5$: C, 60·0; H, 3·6%).

3 : 5 : 8-*Triacetoxy-2-methyl-1 : 4-naphthaquinone*.—Acetylation is best accomplished by treatment with acetic anhydride and a trace of anhydrous zinc chloride, the product being crystallised several times from benzene. After being heated in a vacuum tube in the vapour of boiling toluene to remove acetic acid of crystallisation, the triacetates from both the natural and the synthetic product had m. p. 152—153°, separately or mixed.

73. *The Preparation of Liquid Monomeric Formaldehyde.*

By ROBERT SPENCE and WILLIAM WILD.

LIQUID formaldehyde was first prepared by Kekulé (*Ber.*, 1892, **25**, 2435) and later by Sachs (*Ber.*, 1899, **31**, 1231) by heating paraformaldehyde and condensing the distillate in liquid air. The product melted to an extremely unstable liquid, which polymerised readily to a solid cake of white polyoxymethylene with the evolution of heat. It was shown by Auerbach and Barschall (*Arb. Kais. Gesundh.*, 1907, **27**, 183), however, that paraformaldehyde contains only 94·2% CH_2O, the remainder being water. Later, Trautz and Ufer (*J. pr. Chem.*, 1926, **113**, 105) devised a method for the separation of the water, the condensate in the first trap being allowed to warm very slowly so that the liquid portion ran

to the bottom of the vessel, leaving behind a considerable fraction of polymerised solid, which contained the whole of the water. The liquid was redistilled into a second trap of special form, where a clear specimen finally collected at the bottom. Trautz and Ufer showed that the vapour obtained from the liquid obeyed the gas laws and was indeed monomeric formaldehyde. Their investigation of the polymerisation of the gas has recently been extended by Spence (J., 1933, 1193), who found, however, that Trautz and Ufer's method yielded liquids of varying stability : some remained mobile and transparent on warming to the boiling point, whilst others polymerised with extraordinary vigour. The liquid monomeride has also been obtained in a comparatively stable form by distillation of the alkali-precipitated polyoxymethylene (Walker, *J. Amer. Chem. Soc.*, 1933, **55**, 2821).

Numerous experiments have indicated that the instability of previous preparations from paraformaldehyde might be ascribed (*a*) to the presence in the initially evolved gas of incompletely disintegrated portions of the paraformaldehyde chain, hydrated molecules, etc., which would probably act as centres of polymerisation if present in the liquid ; and (*b*) to the presence of oxygen adsorbed on the walls of the containing vessels. The apparatus shown in the fig. eliminates these factors ; during the past year, it has uniformly given samples of a high order of stability and having no tendency to polymerise explosively.

EXPERIMENTAL.

Paraformaldehyde was prepared by evaporation to dryness of a 40% solution of formaldehyde The product was broken up, dried in a vacuum desiccator over sulphuric acid for 2 days, powdered, and placed in the distillation vessel (30 mm. diameter and 100 mm. long). A thick
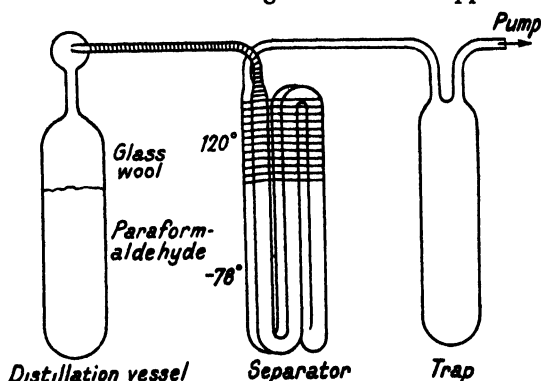
wad of glass wool was introduced to prevent particles of the solid being carried over into the condensing system during the distillation, and the vessel was sealed to the apparatus as shown in the fig The separator vessel consisted of a 10-mm. tube folded into three U-tubes in a compact block (20 cm. long), the upper part of which was wrapped with nichrome wire and asbestos This, together with the tube leading to the distillation vessel, was maintained at 100—120°, and the lower, unwrapped portion immersed in carbon dioxide–ether The system was first pumped out by a mercury-diffusion pump, and the condensing vessels heated with a Bunsen flame Distillation was begun by heating the paraformaldehyde vessel to 110° in an oil-bath. During the removal of the first fraction by the pump, the condensing vessels were heated in a blow-pipe flame. It will be shown in a forthcoming paper that formaldehyde reacts rapidly with oxygen adsorbed on glass at 300°, so the above treatment should be such as effectively to free the surface from oxygen. The trap was now cooled in liquid air, and the stop-cock leading to the pump shut off. As the distillation proceeded, the rate gradually became slower and the temperature of the oil-bath could with advantage be raised to 120°. When sufficient solid had collected in the trap, the oil-bath was removed, the apparatus once more connected to the pump, and the trap carefully sealed off from the separator. By alternately removing and replacing the liquid air, the solid was allowed to melt and run to the bottom. The purity and stability of this first condensate suffice for most purposes, but specimens intended for measurements of physical properties were subjected to a second fractionation.

The preparation could be carried out with similar success if the separator vessel was immersed in calcium chloride–ice at −48°, and the trap maintained at −78° by carbon dioxide–ether. In this case, the formaldehyde condensed to a clear mobile liquid which slowly gelatinised if kept at −78°, and at the end of a fortnight, no liquid was visible. The condensate in the first tube of the separator appeared to consist of a concentrated aqueous solution of formaldehyde The second U-tube generally contained a viscous liquid which rapidly polymerised to a white solid, whilst only traces separated in the final trap.

Liquid formaldehyde prepared by this method shows no disposition towards rapid polymerisation. A specimen placed in a paraffin-bath at room temperature will rapidly boil away, leaving

only traces of polymeride. However, if it is kept for several hours at temperatures above —78°, it begins to gelatinise. Clear liquid can at first be freed from the gel by shaking, but the latter becomes stiffer with time and no free liquid can be observed. Nevertheless, such a gel will evolve large quantities of monomeric gas, and when kept until there is no more vaporisation, only a relatively small fraction of the original specimen remains behind as solid polymeride. In the polymerisation of gaseous formaldehyde (Spence, *loc. cit.*), there is no evidence of the formation of any intermediate polymerides of low molecular weight. If the same is true of liquid formaldehyde, the gel system must consist of a solid phase and a pure liquid phase. Such a view would be in agreement with the above results and is entirely supported by measurements of the vapour pressure. All preparations of the liquid, whether clear and mobile, or highly gelatinous, would therefore appear to be equally satisfactory as sources of the pure gas.

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74. *A Rearrangement of* o-*Benzamido-sulphides.*

By CHRISTIAN F. WIGHT and SAMUEL SMILES.

IT has been shown (this vol., p. 181) that in alkaline media the acetyl and the 2-nitrobenzoyl derivative of 2-nitro-2'-aminodiphenyl sulphide undergo rearrangement, whereas under the same conditions the picryl and the benzenesulphonyl derivative yield only their alkali salts. This divergent behaviour was ascribed to the influence of the *N*-substituents and, taking the view that rearrangements of the type (I) → (II) are intramolecular displacements, it was pointed out that rearrangement should be favoured in cases such as the acetyl and the nitrobenzoyl derivatives where the acyl groups are provided by relatively weak acids. This requirement of theory has been further confirmed by examination of several other amides of the latter type; the behaviour of the formyl and the benzoyl derivatives may be recorded as typical. In presence of alkali hydroxide rearrangement of the formyl derivative is accompanied by deacylation, the thiol (III) being formed; this was isolated as the disulphide and *S*-methyl derivative. The benzamido-sulphide (I, Ac = $C_6H_5 \cdot CO \cdot$) yielded the benzoyl derivative of (III), which was isolated after methylation; oxidation of the methyl


(I.) (II.) (III.)
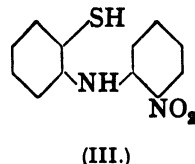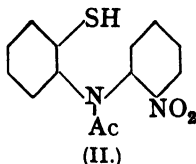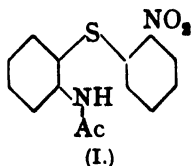
sulphide and subsequent hydrolysis of the *N*-benzoyl sulphone yielded a methyl sulphone of known structure. These examples serve to illustrate the fact that after rearrangement of the mononitro-sulphides (I) the simple thiols or their *N*-acyl derivatives (II) are generally obtained; but in cases derived from (I) by further substitution in the nitrophenyl nucleus the thiols may be rapidly converted into thiazines by loss of nitrous acid in the alkaline medium required for rearrangement. The picryl derivative (VII) affords an interesting example of this behaviour, since it was the subject of a controversy which remained unsettled. Kehrmann (*Ber.*, 1911, **44**, 3012) by reduction of bis-2-picramidophenyl disulphide obtained the corresponding thiol (IV), which with alkali yielded a dinitrothiodiphenylamine (V). Möhlau and his co-workers (*Ber.*, 1910, **43**, 927; 1912, **45**, 131), with the object of

(IV.) (V.) (VI.)
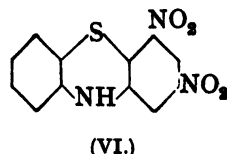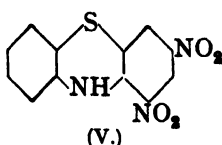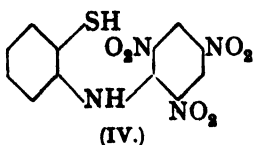
obtaining the isomeric dinitrothiodiphenylamine (VI), converted 2-benzamidophenylthiol into the *S*-picryl derivative by reaction with picryl chloride in presence of sodium acetate.

The product yielded with alkali the *N*-benzoyl derivative of a dinitrothiazine which was identical with (V). No satisfactory explanation of this unexpected result has hitherto been forthcoming; Kehrmann (*Ber.*, 1913, 46, 3014), however, found that the picryl derivative obtained by the method of Möhlau is impure and suggested that the chief product of the process is the *N*-benzoyl derivative of the thiol (IV). Re-examination of the material has now shown that it usually contains at least three substances in varying proportions, but the chief component, which is obtained in a purer state by the use of magnesium carbonate instead of sodium acetate, is neither a thiol nor a disulphide and has accordingly the structure (VII) assigned to it by Möhlau. The implied conclusion that picrylation of 2-benzamidophenylthiol takes place at sulphur in preference to the amido-nitrogen is confirmed by the fact that the dinitro-sulphide (VIII) is obtained either by benzoylation of 2 : 4-dinitro-2'-aminodiphenyl sulphide or from 2-benzamidophenylthiol by reaction with 2 : 4-dinitrochlorobenzene in presence of magnesium carbonate. It is now evident that the formation of the *N*-benzoyl-thiazine (compare V) by the method of Möhlau from the sulphide (VII) consists in a preliminary intramolecular change which yields the *N*-benzoyl derivative of the thiol (IV), followed by conversion of the latter into the thiazine by loss of

(VII.)   (VIII.)   (IX.)
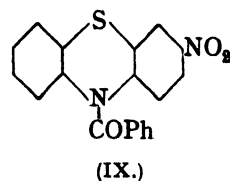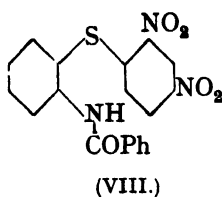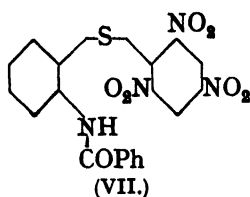
nitrous acid in the alkaline medium as in Kehrmann's process. The 2-acetamidophenyl picryl sulphide (compare VII) similarly yields the dinitro-thiazine (V).

According to previous experiments (J., 1934, 422) and others recently made with rearrangements of this general type, increase in the positive character of the carbon atom from which the sulphur is displaced greatly facilitates the process. Accordingly rearrangement of these sulphides containing the strongly positive picryl nucleus proceeds rapidly in the alkaline media provided by sodium acetate or pyridine, which are without effect on the mono- and di-nitro-derivatives. Thiazine formation is not restricted to the picryl sulphides. The thiol derived from the dinitro-sulphide (VIII) by rearrangement with alkali hydroxide could not be isolated in a pure condition, since it was converted by the reagent into a thiazine. The structure (IX) accordingly ascribed to the latter has since been confirmed in the course of another series of experiments.

EXPERIMENTAL.

2-Nitro-2'-formamidodiphenyl sulphide was obtained by boiling a solution of the amine in formic acid (98%); it formed pale yellow needles from propyl alcohol, m. p. 143° (Found : C, 56·8; H, 3·8. $C_{13}H_{10}O_3N_2S$ requires C, 56·8; H, 3·6%). Alcoholic sodium ethoxide (*N*, 1 mol.) was added in small portions to a hot solution (10%) of this formyl derivative in alcohol; after each addition sufficient methyl iodide was added to remove the red colour previously produced by the alkaline reagent. When the solution was cooled, 2-*o*-nitrophenylaminophenyl methyl sulphide separated; this had m. p. 98° and was identified by comparison with an authentic sample (Found : C, 59·9; H, 4·6; N, 10·7. Calc. : C, 60·0; H, 4·6; N, 10·7%) and by oxidation to the corresponding sulphone (this vol., p. 186). Rearrangement of this formamidosulphide was also conducted (1 mol. of *N*-alcoholic sodium hydroxide) without the addition of methyl iodide. When hydrogen peroxide was added to the diluted product, bis-2-*o*-nitrophenylaminophenyl disulphide (*loc. cit.*) separated (40% yield), m. p. 151° after purification from acetic acid (Found : C, 58·4; H, 3·8. Calc. : C, 58·7; H, 3·6%) and was identified in the usual way.

2-Nitro-2'-benzamidodiphenyl sulphide was obtained from the amine and benzoyl chloride in pyridine; it formed lemon-yellow needles from propyl alcohol, m. p. 106° (Found : C, 64·9; H, 4·0. $C_{19}H_{14}O_3N_2S$ requires C, 65·1; H, 4·0%). Rearrangement of this sulphide was effected in boiling alcohol by the gradual addition of alcoholic sodium hydroxide (*N*, 1·3 mols), methyl iodide being added as in the case of the formyl derivative.

2-o-Nitrophenylbenzamidophenyl methyl sulphide separated when the reacting mixture was cooled, it gave methyl mercaptan when warmed with hydriodic acid and separated from acetic acid in yellow needles, m. p. 206° (Found : C, 65·8; H, 4·3; N, 7·7. $C_{20}H_{16}O_3N_2S$ requires C, 65·9; H, 4·4; N, 7·7%). A small quantity of 2-o-nitrophenylaminophenyl methyl sulphide (*loc. cit.*) was isolated from the residues of this process.

2-o-Nitrophenylbenzamidophenylmethylsulphone was obtained by oxidising the above methyl sulphide with hydrogen peroxide in the usual manner; it formed plates from acetic acid, m. p. 251° (Found : C, 60·6; H, 4·1. $C_{20}H_{16}O_5N_2S$ requires C, 60·6; H, 4·0%).

The preceding substance was also obtained from the rearrangement of 2-*nitro*-2'-*benzamido-diphenylsulphone*, which formed plates from acetic acid, m. p. 139°, and was isolated by oxidising the sulphide with excess of hydrogen peroxide in hot acetic acid (Found : C, 59·4; H, 3·7. $C_{19}H_{14}O_5N_2S$ requires C, 59·7; H, 3·6%). Rearrangement of this sulphone took place rapidly when an alcoholic solution containing sodium hydroxide (1·25 mols.) was boiled. The structure of the sulphinic acid thus formed was shown (a) by isolating it and removing the sulphinic group by successive treatment with mercuric chloride and hydrochloric acid (this vol., p. 181); the product had m. p. 76° and was identical with 2-nitrodiphenylamine; (b) by methylation in the alkaline solution obtained after rearrangement. The product of this process had m. p. 251° and was identical with the 2-o-nitrophenylbenzamidophenylmethylsulphone obtained by oxidising the sulphide; removal of the benzoyl group from this was effected by boiling the solution in acetic acid containing sulphuric acid (20%). The resulting material was identified as 2-o-nitrophenylaminophenylmethylsulphone by comparison with an authentic specimen (*loc. cit.*).

2 : 4-*Dinitro*-2'-*benzamidodiphenyl sulphide* (VIII) was obtained (a) when the amine and benzoyl chloride (1 mol.) were boiled in acetone (30 mins.). It formed pale yellow needles from acetic acid, m. p. 178° (Found : C, 57·3; H, 3·6; N, 10·6. $C_{19}H_{13}O_5N_3S$ requires C, 57·7; H, 3·3; N, 10·6%). The same substance was obtained in presence of pyridine or sodium acetate. (b) Bis-2-benzamidophenyl disulphide (1 mol.) was reduced in the usual way by a warm aqueous alkaline solution of sodium sulphide. The thiol was liberated from the alkaline solution and dissolved in chloroform. When alcohol containing 2 : 4-dinitrochlorobenzene (2 mols.) and sodium acetate (2 mols.) was added to this chloroform solution, the required sulphide (m. p. 178°) was soon formed (80%).

Rearrangement of this sulphide (4 g.) took place rapidly in boiling acetone (100 c.c.) to which an alcoholic solution of sodium hydroxide (*N*, 1 mol.) had been added. Attempts to isolate the thiol formed as the methyl sulphide by concurrent methylation failed on account of the rapid formation of the thiazine (IX). 3-*Nitro*-6-*benzoylthiodiphenylamine* was isolated (25%) by removing most of the acetone and adding cold alcohol to the residue; it separated from alcohol in yellow prisms, m. p. 161—162° (Found : C, 65·2; H, 3·5; N, 8·2. $C_{19}H_{13}O_3N_3S$ requires C, 65·5; H, 3·4; N, 8·0%).

2-*Benzamidophenyl Picryl Sulphide* (VII).—The product prepared by the method of Möhlau (*loc. cit.*) usually had m. p. 170—190°. Fractionation of this yielded (1) 2-benzamidophenyl disulphide, m. p. 141°, (2) 2 : 4-dinitro-6-benzoylthiodiphenylamine, m. p. 210° (Möhlau, *loc. cit.*), and (3) the required *sulphide*, which separated from acetic acid in orange needles, m. p. 213—214° (decomp.) (Found : C, 51·5; H, 3·1; N, 12·8; S, 7·1; *M*, 435. $C_{19}H_{12}O_7N_4S$ requires C, 51·8; H, 2·7; N, 12·7; S, 7·3%; *M*, 440). This was more readily obtained in a pure condition by adding a cold chloroform solution of 2-benzamidophenylthiol (1 mol.) to ether which contained picryl chloride (1 mol.) in presence of magnesium carbonate, free access of air to the mixture being prevented. After 1 hour, the insoluble material was collected and washed with acetic acid and then with water; the crude product remaining (50%) had usually m. p. about 208—211°. The substance did not exhibit the usual reactions of a thiol; in boiling alcohol it was converted by (1) pyridine (90% yield), (2) sodium acetate (92% yield), (3) sodium hydroxide (1 mol.) (80% yield) into 2 : 4-dinitro-6-benzoylthiodiphenylamine, m. p. 210° (Found : C, 57·9; N, 11·0. Calc. : C, 58·0; N, 10·7%), described by Möhlau (*loc. cit.*); conversion of the latter by hydrolysis into the 3 : 5-dinitrothiodiphenylamine (V, m. p. 189°) obtained by Kehrmann (*loc. cit.*) from 2-picramidophenylthiol was confirmed.

2-*Acetamidophenyl Picryl Sulphide*.—An alkaline aqueous solution of 2-acetamidophenyl-thiol was prepared from the disulphide by reduction with sodium sulphide in the usual manner. The thiol was liberated from the solution of the sodium salt by addition of dilute acid, care being taken to avoid excess of the latter; it was dissolved in chloroform and the cold solution was added to ether which contained picryl chloride and excess of magnesium carbonate. Access of air to the mixture was prevented; the product was slowly precipitated in the crystalline state.

Inorganic material was removed from the solid as usual and the residue was purified from ethyl acetate. It formed orange needles, m. p. 215—216° (decomp.) (Found : C, 44·5; N, 14·8; S, 8·3; *M*, 384. $C_{14}H_{10}O_7N_4S$ requires C, 44·4; N, 14·8; S, 8·5%; *M*, 378). A boiling solution of this substance in acetone which contained alcoholic sodium hydroxide (1 mol.) yielded the 3 : 5-dinitro-thiazine (V), deacetylation having taken place during the process. Prolonged treatment (2 hours) with a boiling alcoholic solution (20%) of pyridine yielded a small quantity of the thiazine (V) together with bis-2-picramidophenyl disulphide.

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75. *Chemical Constitution and the Dissociation Constants of Monocarboxylic Acids. Part III.*

By J. FREDERICK J. DIPPY, FRANK R. WILLIAMS, and (in part) REGINALD H. LEWIS.

THE dissociation constants of a number of substituted benzoic acids have been redetermined, since earlier values are not now acceptable in view of the experimental and theoretical developments in the subject. The results are recorded in Table I, together with Λ_0 data. The practical methods and calculation of the results were those described in previous papers (Parts I and II; J., 1934, 161, 1888).

TABLE I.

Acid.	Λ_0 (Na salt).		Mean Λ_0 (acid).	$K_{class} \times 10^5$.	$K_{therm} \times 10^5$.
p-Fluorobenzoic	82·7,	83·5	382·7	7·39	7·22
o-Chlorobenzoic	84·5,*	84·6 *	384·1	119	114
m-Chlorobenzoic	80·75,*	81·25 *	380·6	15·2	14·8
p-Chlorobenzoic	82·3,*	82·3 *	381·9	10·7	10·5₅
o-Bromobenzoic	80·2,*	80·8	380·1	146	140
p-Bromobenzoic	79·8,*	80·1 *	379·6	10·8	10·7
p-Aminophenylacetic	79·4,	80·4	379·5	(see Table III)	

* These values were obtained with solutions prepared from specimens of solid salt.

The following are earlier constants for aqueous solutions at 25° :

p-*Fluorobenzoic acid* : $K_{class.} \times 10^5 = 14$ (Slothouwer, *Rec. trav. chim.*, 1914, 33, 324).

o-*Chlorobenzoic acid* : $K_{class.} \times 10^5 = 132$ (Ostwald, *Z. physikal. Chem.*, 1889, 3, 418); 128—135 (Schaller, *ibid.*, 1898, 25, 522; the value being erroneously ascribed to *p*-chlorobenzoic acid); 128 (Kendall, J., 1912, 101, 1275); 121—138 (Whiteman and Jones, *Amer. Chem. J.*, 1911, 46, 93); $K_{therm.} \times 10^5 = 119·7$ (Saxton and Meier, *J. Amer. Chem. Soc.*, 1934, 56, 1918).

m-*Chlorobenzoic acid* : $K_{class.} \times 10^5 = 15·5$ (Ostwald, *loc. cit.*); 15·3—15·9 (Smith and Jones, *Amer. Chem. J.*, 1913, 50, 28); $K_{therm.} \times 10^5 = 15·06$ (Saxton and Meier, *loc. cit.*).

p-*Chlorobenzoic acid* : $K_{class.} \times 10^5 = 9·3$ (Ostwald, *loc. cit.*); 7·8 (Smith and Jones, *loc. cit.*); $K_{therm.} \times 10^5 = 10·4$ (Saxton and Meier, *loc. cit.*).
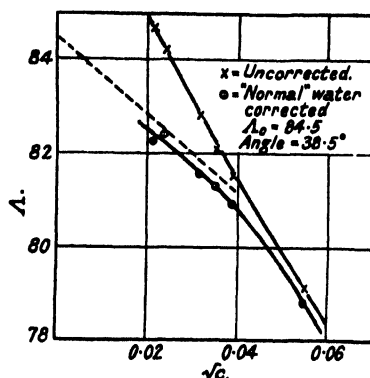
o-*Bromobenzoic acid* : $K_{class.} \times 10^5 = 145$ (Ostwald, *loc. cit.*); 140—180 (Smith and Jones, *loc. cit.*).

Values of $K_{therm.}$ for *o-*, *m-*, and *p*-chlorobenzoic acids were published by Saxton and Meier (*loc. cit.*) after the completion of our measurements. Those for the *m-* and *p*-acids agree with our values to within 2%, and even these small differences are capable of some explanation. In computing $K_{therm.}$ for the former acid, Saxton and Meier employed an extrapolation method; if, however, their value had represented the mean of the constants derived for the various concentrations (as in our procedure), a value of $1·497 \times 10^{-4}$ would have been obtained. Their constant for the sparingly soluble *p*-acid was derived from two determinations only, and hence our value, the result of observations on *fifteen* solutions, is obviously more reliable. Ostwald's measurement was upon a single solution.

The Λ_0 (acid) values obtained for chlorobenzoic acids by Saxton and Meier are as follows : *o-*, 379·96; *m-*, 380·67. They did not conduct measurements on sodium *p*-chlorobenzoate, but accepted for Λ_0 (acid) the value accorded to benzoic acid; this provisional value is precisely the same as that obtained by us from actual measurements. Excellent agreement

with Saxton and Meier is reached in the case of sodium *m*-chlorobenzoate, but with sodium *o*-chlorobenzoate there is a discordance, and this partly accounts for the 5·6% disagreement between the $K_{therm.}$ values.   There is no question of differences in the accepted sodium- and hydrogen-ion mobilities, since Saxton and Meier also use MacInnes, Shedlovsky, and Longsworth's values (*J. Amer. Chem. Soc.*, 1932, **54**, 2758).   Our method of computing Λ_0 (salt) was that described in Part II ; the fig. shows a graph of measurements with sodium *o*-chlorobenzoate, the data being in Table II.   Details for this salt are given in view of the aforementioned serious discordance.

One very significant feature of the present measurements is the order of strengths of the *p*-monohalogenobenzoic acids.   This is Br>Cl>F, *i.e.*, the converse of the order exhibited by the halogenoacetic acids; the order of the constants for three *p*-halogeno-phenylacetic acids (Part I) was similar, *viz.*, I>Br>Cl.   Measurements on *p*-fluorophenyl-acetic acid alone have since been conducted, and taking, for the present, a value of Λ_0 (acid) = 382, a thermodynamic constant of $5·68 \times 10^{-5}$ is obtained, pointing to a relatively large fall in strength as in the case of *p*-fluorobenzoic acid (see Table I).   There is every reason to believe that the final correct value for $K_{therm.}$ will not differ from the provisional value by more than 2%.   This work provides the first conclusive demonstration of the inversion of the order of the halogens as shown in the strengths of aromatic carboxylic acids; the conclusion could not safely have been reached from the data available hitherto, even from the comparatively recent work of Kuhn and Wassermann (*Helv. Chim. Acta*, 1928, **11**, 31), who investigated all twelve monohalogenobenzoic acids in 50% aqueous methyl alcohol (see p. 346).

In the *o*-substituted benzoic and phenylacetic acids also, the bromo- is stronger than the chloro-acid, but perhaps more striking still is the fact that, although *o*-chloro- and *o*-bromo-benzoic acids are of the order of ten times as strong as their *m*- and *p*-isomerides, the monochloro- and monobromo-phenylacetic acids are all of comparable strengths.

The conductivity of *p*-aminophenylacetic acid has been measured because it was considered that it might be of use in connexion with the problem of amphoteric electrolytes.   The values of $K_{class.}$, when arranged in the order of diminishing concentration of the solutions, present a steady fall until a concentration of about 0·0015N is reached; with further dilution an abnormal increase in acid strength occurs.

The Effect of Substituents on the Mobilities of Anions.—The only generalisations which can be made from the data of the 23 systems so far studied are that the methoxy- and nitro-substituted aromatic anions have relatively low speeds of migration, and also that the halogen- or nitro-substituted isomeric ions possess distinctly different speeds, dependent upon the position of the substituent.

EXPERIMENTAL.

The measurements, as hitherto, were conducted on aqueous solutions at 25°.   Difficulty was encountered in preparing the initial stock solutions of the sparingly soluble *p*-chloro- and *p*-bromo-benzoic acids.   Several hours' standing in the thermostat and vigorous intermittent shaking were necessary; this unavoidable delay did not have any effect.   In the case of the above acids, and of *o*- and *m*-chlorobenzoic acids, 500 c.c. of initial solution were prepared (compare *p*-anisic acid; Part II).   The time taken to dissolve different acids is not wholly dependent upon their maximum solubilities, since appreciably soluble substances dissolve at vastly different rates.   In order to hasten complete solution, the specimens were always well pulverised in an agate mortar before weighing.

The solubilities of *p*-iodobenzoic and *p*-benzamidophenylacetic acids were so small as to preclude measurements.

Two expeditious items of procedure recently adopted by workers elsewhere are comparable

with those employed by us. As an alternative to the weight-burette method of dilution, Brockman and Kilpatrick (*J. Amer. Chem. Soc.*, 1934, **56**, 1483) have followed a procedure in which a series of weighed flasks is required (compare Part I, p. 163). Also, Saxton and Meier (*loc. cit.*; cf. Saxton and Langer, *ibid.*, 1933, **55**, 1780), in their sodium salt investigations, prepared the solutions accurately by titration, and avoided the isolation of the solid salt; their choice of alkali (sodium carbonate), however, raises a definite objection.

TABLE II.

Sodium o-chlorobenzoate.

$\kappa = 1 \cdot 0$ gemmho.   Cell constant $= 0 \cdot 07243$.

$10^3 C$	2·923	1·522	1·242	0·9575	0·5575	0·4421
Λ (uncorr.)	79·18	81·56	82·12	82·85	84·33	84·62
Λ (corr.)	78·83	80·91	81·36	81·68	82·45	82·35

TABLE III.

Cell constant.	$10^3 C$.	Λ.	$K \times 10^5$ (class.).	$K \times 10^5$ (therm.).	Cell constant.	$10^3 C$.	Λ.	$K \times 10^5$ (class.).	$K \times 10^5$ (therm.).
	p-*Fluorobenzoic acid.*					o-*Chlorobenzoic acid.*			
0·07288	4·003	48·70	7·43	7·18	0·1367	6·011	138·0	121	114
	2·250	63·52	7·43	7·22		4·211	158·0	121	115
	1·508	75·88	7·39	7·20		3·529	168·6	121	115
	0·9448	92·87	7·35	7·19		2·742	182·5	118	113
	0·5832	113·4	7·27	7·15		1·640	214·2	116	112
0·07288	3·468	52·14	7·45	7·21	0·1367	3·714	165·2	121	115
	2·263	63·27	7·41	7·20		2·856	180·5	119	114
	1·718	71·27	7·32	7·13		2·228	196·3	119	115
	0·4657	124·3	7·27	7·15		1·507	220·9	118	114
	0·1730	181·2	7·36	7·27	0·07288	1·139	238·6	116	114
0·07288	2·874	56·98	7·49	7·25		0·5258	284·7	(112)	(111)
	1·812	70·33	7·50	7·30	0·1367	2·947	178·8	120	115
	1·246	82·94	7·47	7·29		1·963	204·5	119	115
	0·7372	103·9	7·44	7·31		1·238	234·0	118	115
	0·2444	159·6	7·29	7·20	0·07288	0·7084	267·7	114	112
						0·3261	309·1	(109)	(109)
	m-*Chlorobenzoic acid.*					p-*Chlorobenzoic acid.*			
0·07288	1·179	114·5	15·2	14·8	0·07288	0·3886	153·9	10·6	10·4
	0·8439	131·1	15·3	14·9		0·3591	159·5	10·8	10·6
	0·7546	137·2	15·3	15·0		0·3113	168·3	10·8	10·6
	0·5937	150·2	15·3	15·0		0·2801	174·4	10·8	10·6
	0·4081	172·0	15·2	14·9		0·2256	189·2	(11·0)	(10·8)
	0·1668	227·4	(14·8)	14·7		0·1710	205·9	10·8	10·7
0·07288	1·203	113·4	15·2	14·8	0·07288	0·3642	157·9	10·6	10·5
	0·8139	132·4	15·1	14·8		0·3335	163·1	10·6	10·5
	0·7000	140·5	15·1	14·8		0·2868	170·4	10·7	10·5
	0·4910	161·4	15·3	15·0		0·2259	188·2	10·8	10·7
	0·4162	170·7	15·2	14·9		0·1967	196·6	10·8	10·6
0·07288	1·296	109·1	15·0	14·6		0·1607	210·4	10·9	10·7
	0·8426	130·5	15·1	14·7	0·07288	0·3297	164·6	10·8	10·6
	0·7011	140·5	15·1	14·8		0·3021	168·2	10·5	10·4
	0·5606	153·1	15·2	14·9		0·2748	174·4	10·5	10·4
	0·5046	159·0	15·1	14·8		0·2122	190·5	10·5	10·4
						0·1852	198·4	(10·4)	(10·3)
	o-*Bromobenzoic acid.*					p-*Bromobenzoic acid.*			
0·07305	3·413	181·3	149	142	0·07288	0·2030	192·8	10·6	10·5
	2·468	200·9	146	140		0·1838	201·2	11·0	10·8
	1·199	247·3	145	142		0·1724	205·6	11·0	(10·9)
	0·9356	263·6	147	(144)		0·1527	211·8	10·7	10·7
0·07305	4·662	161·7	147	139	0·07288	0·1901	197·8	10·8	10·6
	2·776	193·2	146	140		0·1787	201·8	10·8	10·7
	1·762	223·0	147	141		0·1632	208·5	10·9	10·8
	0·7370	275·1	140	139		0·1495	214·3	10·9	10·8
0·07305	5·077	159·3	(154)	(144)		0·1485	214·4	10·9	10·7
	3·317	182·5	147	140	0·07288	0·1891	198·0	10·8	10·6
	3·280	182·6	146	139		0·1578	208·8	10·6	10·5
	0·8360	269·2	144	142		0·1252	224·8	10·8	10·7

Cell constant.	10³ C.	Λ.	K × 10⁶ (therm.).	Cell constant.	10³ C.	Λ.	K × 10⁶ (class.).
	p-Fluorophenylacetic acid.				*p-Aminophenylacetic acid.**		
0·07243	1·943	60·71	5·69	0·07355	3·084	10·99	0·267 (a)
	1·153	76·78	5·70		2·302	12·58	0·262
	1·000	81·51	5·66		2·209	12·87	0·263 (c)
	0·6995	94·81	5·62		2·195	12·91	0·263 (a)
	0·3518	126·0	5·63		1·714	14·34	0·255 (b)
	0·2031	153·8	(5·44)		1·663	14·60	0·256 (c)
0·07243	2·678	52·72	5·75		1·493	15·21	0·250
	1·602	66·71	5·77		1·144	17·38	0·251
	1·220	75·11	5·74		1·131	17·56	0·254
	0·8339	88·57	5·71		1·127	17·88	0·263
	0·5538	105·7	5·75		0·8279	20·93	0·267
	0·4209	153·8	5·62		0·8147	21·24	0·271
0·07243	0·8260	88·76	5·69		0·7993	21·50	0·271 (b)
	0·5129	108·0	5·61		0·6409	24·75	0·292 (c)
	0·2522	143·2	5·60				
	0·1713	165·4	5·62				

* In this case the three runs, *a*, *b*, and *c*, have been combined; no thermodynamic constants have been calculated, since the $K_{class.}$ values are themselves only apparent.

The values in parentheses were not included in the calculation of the averages given in Table I.

Preparation and Purification of Materials.—The chloro- and bromo-benzoic acids were all purchased from Messrs. British Drug Houses Ltd. Where the m. p.'s were below the best value recorded, preliminary crystallisations from water, sometimes containing acetone, were conducted, with animal charcoal if necessary. The final purification was carried out in the usual way with conductivity water. A variety of m. p.'s is given in the literature for most of these acids but, with one exception, each of our final specimens possessed the highest value.

o-Chlorobenzoic acid, 142° (Fels, *Z. Kryst.*, 1903. **37**, 485, 142°).

m-Chlorobenzoic acid, 158° (Montagne, *Rec. trav. chim.*, 1900, **19**, 52, 158°).

p-Chlorobenzoic acid, 241° (Fels, *Z. Kryst.*, 1900, **32**, 389, 243°; Müller, *Z Chem.*, 1869, **137**, 235°).

o-Bromobenzoic acid, 150° (Rhalis, *Annalen*, 1879, **198**, 102, 150°).

p-Bromobenzoic acid, 254—255° (Flaschner and Rankin, *Monatsh.*, 1910, **31**, 44, 254°).

Kuhn and Wassermann (*loc. cit.*) used all the above acids in their investigation, but the m. p.'s (uncorr.) recorded by them are consistently lower than ours. This deficiency, in addition to the fact that they did not carry out their measurements at one fixed temperature, doubtless contributes to the irregularity of their results.

p-Fluorobenzoic acid, m. p. 182°, was obtained by the hydrolysis of its ethyl ester (Dippy and Williams, J., 1934, 1466) (Slothouwer, *loc. cit*, records m. p. 182°).

The preparation of *p*-fluorophenylacetic acid, m. p. 86°, has already been described (Dippy and Williams, *loc. cit.*).

p-Aminophenylacetic acid was obtained by the reduction of the *p*-nitro-acid with ferrous sulphate in the presence of ammonia (Jacobs and Heidelberger, *J. Amer. Chem. Soc.*, 1921, **43**, 180). After several recrystallisations from water (charcoal), the acid separated in almost colourless leaves, m. p. 200°. In earlier work the reduction was conducted far less successfully by the stannous chloride method.

THE TECHNICAL COLLEGE, CARDIFF.   [*Received, January 16th,* 1935]

76. *Chemical Constitution and the Dissociation Constants of Mono-carboxylic Acids. Part IV. A Discussion of the Electrolytic Dissociation of Substituted Benzoic and Phenylacetic Acids in Relation to Other Side-chain Processes.*

By J. F. J. DIPPY, H. B. WATSON, and F. R. WILLIAMS.

THE earlier parts of this series (Dippy and Williams, J., 1934, 161, 1888, and preceding paper) contain an account of the determination, by an accurate and rapid method, of the dissociation constants of a number of substituted benzoic and phenylacetic acids in water

at 25°. In the present communication these results are considered in the light of modern electronic conceptions, and in their relationship with other relevant data.

The extensive work of Ostwald (results summarised in *Z. physikal. Chem.*, 1889, **3**, 418) made it clear that substituents may either increase or decrease the strength of a carboxylic acid, and Derick (*J. Amer. Chem. Soc.*, 1911, **33**, 1152) expressed the "negativity" or "positivity" of a group as a logarithmic function of the dissociation constant of the appropriate substituted acid. It was pointed out by Lewis ("Valence and the Structure of Atoms and Molecules," 1923, pp. 85, 139) that the observed effect is due to the electron-attractive or electron-repelling character of the group, but the derivation of a quantitative relationship between acid strengths and the polarities of substituents was not possible before the accumulation of knowledge of dipole moments. It has recently been observed by Nathan and Watson (J., 1933, 893; cf., however, Waters, *Phil. Mag.*, 1929, **8**, 436) that the logarithms of the dissociation constants (Ostwald's values) of a number of substituted acetic acids $CH_2X\cdot CO_2H$ are given by the expression $\log K = \log K_0 - 2\cdot 4(\mu + 0\cdot 032\mu^2)$, where K and K_0 refer to the substituted and unsubstituted acids respectively, and μ (in Debye units) is the dipole moment of the corresponding substituted methane CH_3X. The value of the dissociation constant of diphenylacetic acid (Part I, *loc. cit.*) is in agreement with Nathan and Watson's expression ($10^5 K^*_{class.}$: obs., 11·7; calc., assuming $\mu = -2 \times 0\cdot 39, 11\cdot 46$). The saturated aliphatic monocarboxylic acids thus appear to present an unusually simple case, where the dipole (inductive) effect accounts quantitatively for the changes in acid strength.

A vast number of observations have indicated, however, that the influence of a substituent attached directly to the benzene nucleus is frequently of a complex character. In the realm of aromatic substitution, for example, all neutral, non-ion-forming groups with unshared electrons adjacent to the nucleus (*e.g.*, –OR, –NHAc) are *op*-directive, irrespective of the direction of the dipole (Ingold, *Rec. trav. chim.*, 1929, **48**, 802), and phenomena of this kind, which were formerly related to characters such as the "state of saturation" (Vorländer) or the "affinity demand" (Flürscheim) of the group, are now ascribed to electromeric displacements *away* from the substituent $(+ T)$. Conversely, groups having oxygen doubly linked to the atom attached to the nucleus (*e.g.*, –NO₂, –COR) can give rise to electromeric displacements *towards* the group $(- T)$. In other words, quantum-mechanical resonance is possible between alternative configurations (here benzenoid and quinonoid) of similar energy, and the stable condition of the molecule is actually intermediate between these "unperturbed states" ("mesomerism," Ingold, J., 1933, 1120; *Chem. Reviews*, 1934, **15**, 232). Examples of the operation of this effect are found in the methoxy- and nitro-substituted aromatic acids.

Influence of Methoxyl.—Methylglycollic (33·5) and *m*-methoxybenzoic (8·8) acids are stronger than acetic (1·80) and benzoic (6·0) acids respectively [the values in parentheses are those of $10^5 K_{class.}$, the first, third, and fourth being due to Ostwald, and the other to Pip (Diss., Heidelberg, 1898, quoted from International Critical Tables)], indicating electron-attraction by methoxyl. Ostwald found $10^5 K_{class.}$ for *p*-anisic acid, however, to be 3·2, and the values $10^5 K_{therm.}$ = 3·38 and 6·27 for *p*-anisic and benzoic acids respectively (Part II), obtained by the aid of modern technique and of the Debye–Hückel–Onsager equation, can leave no doubt as to the relatively low dissociation constant in the former case. The order of acid strengths is *m*-OCH₃ > H > *p*-OCH₃, and this is further confirmed by the recent results of Branch and Yabroff (*J. Amer. Chem. Soc.*, 1934, **56**, 2568; $10^5 K_{therm.}$ for benzoic acids in 25% alcohol at 25°; *m*-OCH₃, 2·87; unsubstituted, 2·29; *p*-OCH₃, 1·16). The same order is found in the acetoxybenzoic (*m*-O·CO·CH₃ = 9·9, *p*-O·CO·CH₃ = 4·2; Ostwald), in the ethoxybenzoic (*m*-OC₂H₅ = 9·0, *p*-OC₂H₅ = 5·0; Pip), and in the phenetylboric acids ($10^{10} K_{therm.}$ in 25% alcohol at 25°; *m*-phenetylboric, 3·05; phenylboric, 1·97; *p*-phenetylboric, 0·608; Branch, Yabroff, and Bettmann, *J. Amer. Chem. Soc.*, 1934, **56**,

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* $K_{class.}$ is here quoted, since comparison is made with Ostwald's values, upon which the expression was based. As pointed out by Nathan and Watson, the relative inaccuracy of the older values is here unimportant in view of their wide range.

All dissociation constants referred to in this communication, unless otherwise defined, are for aqueous solutions at 25°.

937). Similarly, Ostwald found values of 8·5 and 5·2 for *m*- and *p*-acetamidobenzoic acids respectively. In all these cases, resonance between alternative configurations * such as (I) and (II), usually expressed as (III), will reduce the strength of the *p*-substituted acid (compare Ingold, *J.*, 1933, 1124; Branch, Yabroff, and Bettmann, *loc. cit.*). Since the
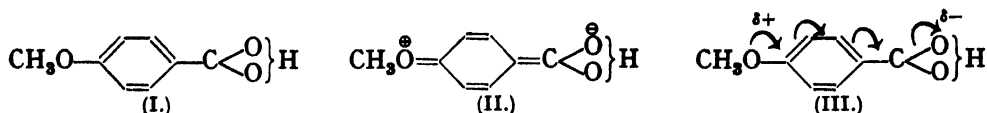
m-quinonoid form is not possible, these groups in the *m*-position exert only the dipole effect, which increases acidity. Similar differences in the influence of *m*- and *p*-methoxyl have been observed in various side-chain reactions such as the hydrolysis and the reduction of benzyl bromides (Lapworth and Shoesmith, *J.*, 1922, **121**, 1394; Shoesmith and Slater, *J.*, 1926, 217), and the alkaline hydrolysis of benzoic esters (Kindler, *Annalen*, 1926, **450**, 3; 1927, **452**, 90).

A depression of acid strength, though of smaller magnitude, is also observed in *p*-methoxyphenylacetic acid [$10^5 K_{therm.}$ = 4·36 (Part II), as compared with 4·88 for phenyl-acetic acid (Part I)]. This would not, perhaps, have been anticipated, since the transmission of the electromeric effect, as such, is rendered impossible by the intervening methylene group. It is simplest to suppose that electromeric displacements, initiated by methoxyl, proceed to the *p*-carbon atom, and that the effect of the resulting fractional negative charge is propagated inductively (or through the medium) to the carboxyl group. The methoxyl group thus exerts " what is virtually a relayed general or inductive effect " (Robinson, *J.*, 1933, 1115). This may be represented as in (IV). Methoxyl in the *m*-position appears again to behave in accordance with its dipole effect, 3 : 4-dimethoxyphenylacetic acid ($10^5 K_{therm.}$ = 4·64, Part II) being somewhat stronger than the *p*-methoxy-acid.

An interpretation akin to that outlined above is applicable to the activating influence of phenyl in the nitration of guaiacol benzyl ether (Allan and Robinson, *J.*, 1926, 376; compare Allan, Oxford, Robinson, and Smith, *ibid.*, p. 407), where the initiation of electromeric displacements by ethereal oxygen is facilitated, and to the effect of *p*-methoxyl upon the reactions of aryl β-chloroethyl sulphides (Baddeley and Bennett, *J.*, 1933, 261), where ionisation of chlorine is facilitated and reaction with iodide ion is retarded.

Influence of Nitroxyl.—In accordance with expectation, the nitro-group, when present in any position, increases very considerably the strength of an aromatic acid ($10^5 K_{class.}$ for *m*- and *p*-nitrobenzoic acids = 34·5 and 39·6 respectively, Ostwald; $10^5 K_{therm.}$ for *m*- and *p*-nitrophenylacetic acids = 10·8 and 14·1, Parts I and II; $10^9 K_{therm.}$ for *m*- and *p*-nitrophenylboric acids in 25% alcohol at 25° = 6·9 and 9·8 respectively, Bettmann, Branch, and Yabroff, *J. Amer. Chem. Soc.*, 1934, **56**, 1865). It has been pointed out by the last-named authors, however, that the dipole effect, if operative alone, would be expected to lead to the order of strengths *m*>*p*, while the reverse is actually the case. This applies to all the pairs of acids referred to above, and, indeed, an inspection of available data shows that the influence of nitroxyl upon side-chain processes is usually greater in the *p*- than in the *m*-position. Bettmann, Branch, and Yabroff ascribe the phenomenon to resonance (− *T*), and it may be pointed out that Opolski and Zwislocki (*Ber.*, 1916, **49**, 1606) assigned the formula $CO_2Et·CH:C_6H_4:NO·OM$ to certain highly coloured salts which they prepared from ethyl *p*-nitrophenylacetate. It is not suggested, of course, that a

* are written for carboxyl and nitroxyl respectively, in view of the resonance

between the structures and (Ingold, *J.*, 1933, 1126; Pauling and

Sherman, *J. Chem. Physics*, 1933, **1**, 606)

hydrogen atom of the methylene group of p-nitrophenylacetic acid is actually free in aqueous solution, but a position such as that represented in (V) would account for the enhanced strength.

The present conception of the T effect renders unnecessary the postulate that it cannot operate *against* the attack of a reagent (compare Baddeley and Bennett, *loc. cit.*, p. 265; Shoppee, J., 1932, 698), and, indeed, numerous examples are available of the operation of resonance as a retarding influence, such as the depression by p-methoxyl of the alkaline hydrolysis of benzoic, phenylacetic, hydrocinnamic, and cinnamic esters (Kindler, *Annalen*, 1927, **452**, 95) and of benzamides (Reid, *Amer. Chem. J.*, 1900, **24**, 397), and of the reaction of aryl β-chloroethyl sulphides with iodide ion (Baddeley and Bennett, *loc. cit.*). Indeed, one cannot ignore the possibility that the powerful deactivation of the o- and p-positions by nitroxyl and carbonyl, leading to m-substitution, may be due, in some way, to resonance; this would render unnecessary the assumption of a p-linkage (Ingold, *Ann. Reports*, 1926, **23**, 133).

Influence of Halogens.—The dissociation constants of the halogen-substituted benzoic and phenylacetic acids fall, as a group, into the anticipated position, the acids being stronger than the unsubstituted, and weaker than the nitro-substituted, acids, $NO_2 > Hal > H$. The order of the halogens among themselves, however, is not that of their inductive effects. The relative strengths of the halogenoacetic acids ($10^3 K_{class.}$: F, 2·17; Cl, 1·55; Br, 1·38; I, 0·71; Scudder, " Conductivity and Ionisation of Organic Compounds," 1914) and the percentages of m-derivative formed in the nitration of the benzyl halides (F, 17·5; Cl, 11·6; Br, 6·6; Flürscheim and Holmes, J., 1928, 1611; Ingold and Ingold, *ibid.*, p. 2253) lead inevitably to the order $F > Cl > Br > I$ for inductive effects. The dissociation constants ($10^5 K_{therm.}$) of the p-halogenoaromatic acids, however, are as follows (Parts I and III) :

> Benzoic : p-F, 7·22; p-Cl, 10·55; p-Br, 10·7.
> Phenylacetic : p-F, 5·68 *; p-Cl, 6·45; p-Br, 6·49; p-I, 6·64.

The values for the chloro- and bromo-acids are, of course, scarcely distinguishable, but the general sequence is clear, and it is the reverse of that to which the inductive effects would lead. A similar inversion has been found in the strengths of the halogenophenylboric acids ($10^{10} K_{therm.}$: p-F, 3·66; p-Cl, 6·30; p-Br, 7·26; Bettmann, Branch, and Yabroff, *loc. cit.*), and in a number of side-chain reactions (see lists given by Baddeley and Bennett, *loc. cit.*, and by Nathan and Watson, J., 1933, 1248; an additional example has recently been observed by Davies and Lewis, J., 1934, 1599). Allied problems are presented by the values of the dipole moments of the halogenobenzenes and by the op-directive influence of the halogens. It is clearly necessary to postulate a displacement of electrons opposite in direction to the inductive effect; this must be permanent, to some degree at least, since it is evident in the measured moments of the halogenobenzenes. We are in agreement with Baddeley and Bennett's conclusion (*loc. cit.*; compare Bennett, J., 1933, 1112) that the phenomenon of inversion requires for its interpretation an effect which diminishes in magnitude in the order $F > Cl > Br > I$ (compare Bettmann, Branch, and Yabroff, *loc. cit.*, who, however, suggest that this is the " resonance order "). It seems inevitable, however, that, of the four halogens, fluorine must control its electrons most powerfully, and iodine, with the largest atom, least powerfully, and for this and other reasons (also pointed out by Baddeley and Bennett) it is difficult to accept the view that the halogens can initiate electromeric displacements by a mechanism similar to that which has proved adequate to interpret the influence of groups such as alkoxyl and dialkylamino. In support of this conclusion, it may be pointed out that, whereas p-halogen substituents *decrease* the speed of acid-catalysed prototropy of acetophenone strictly in accordance with the order of inductive effects (Nathan and Watson, J., 1933, 890), Mr. V. G. Morgan, working in these laboratories, has shown that the substitution of methoxyl in the p-position results in a very considerable *increase* of speed.

It has been pointed out by Burton and Ingold (*Proc. Leeds Phil. Soc.*, 1929, **1**, 424) that " the aryl group contains an available mechanism for the extensive distribution of

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* See preceding paper, p. 344, regarding this value.

an ionic charge of either sign," and Baddeley and Bennett (*loc. cit.*) consider that, since this is the case, a halogen atom attached to the nucleus becomes a partial negative pole, the positive equivalent being largely distributed throughout the nucleus. They thus arrive at the conception of a "reversed field," resulting in the initiation of electromeric displacements which are transmitted to the *o*- and *p*-positions, their magnitude decreasing in the required order, *viz.*, that of inductive effects. The application of this view provides an explanation of the inverted order of the dissociation constants of the *p*-halogeno-benzoic and -phenylacetic acids, as compared with those of the corresponding acetic acids.

In the latter case, there is no mechanism for the distribution of the positive charge residing upon the carbon end of the C–Hal dipole, and the relationship between acid strength and dipole moment is thus a simple and quantitative one, as observed by Nathan and Watson. The inverted order when halogen is attached to the benzene nucleus arises from the distribution of the positive charge, for the resulting "reversed field" mechanism leads to a decrease in acidity. The main influence is still the inductive effect of the halogen, since all the dissociation constants are considerably higher than those of the unsubstituted acids, but on this is superimposed, as a "fine adjustment," the opposing effect of the reversed field, which decreases in the order F>Cl>Br>I and is of sufficient magnitude to invert the order of the halogens among themselves.

It must be emphasised that the view here adopted does not forecast inversion in *every* case where halogens are attached to aryl groups. Although the electromeric displacements set up by the reversed field are to some extent permanent, they are nevertheless dependent upon the *polarisability* of the nucleus, and their magnitude is governed by the extent to which they are permitted or favoured by external conditions, attacking reagents, and groups inside the molecule. Thus, in the acid hydrolysis of *p*-fluorobenzyl bromide (Shoesmith and Slater, *loc. cit.*), they are sufficiently powerful even to outweigh the inductive effect of the halogen, while in the acid-catalysed prototropy of substituted acetophenones their influence is so unimportant that the strict order of inductive effects is followed. It is not surprising, indeed, that the halogens sometimes show a normal and an inverted sequence in different reactions of the same compounds (Baddeley and Bennett, *loc. cit.*). Cases of a partial inversion, too, are not unexpected, and reference may be made to the order of the dipole moments of the halogenobenzenes, *viz.*, Cl>Br>F>I; all the values indicate a permanent displacement of charges which affects the electrical centres of positive and negative electricity in such a way as to reduce the resultant moment (Sutton, *Proc. Roy. Soc.*, 1931, **188**, 686), but only in fluorobenzene is this effect sufficiently great to change the *order* of the values. Other cases of partial inversion are quoted by Shoppee (*J.*, 1933, 1119). It is not possible to forecast the order of reactivities of halogen-substituted benzene derivatives in any particular case, since no means exists for determining the effect of a given set of conditions, internal and external, upon the polarisability of the nucleus.

Although the conception of the "reversed field" is not free from difficulties, we feel that the application of Baddeley and Bennett's ideas leads to an interpretation which fits the facts more closely than does the more conventional assumption of covalency increase between halogen and nuclear carbon. It is, of course, possible, that a completely satisfactory solution of this and many other problems will emerge only after the further development of the wave-mechanical conception of molecular orbitals.

THE TECHNICAL COLLEGE, CARDIFF.

77. *The Kinetics of the Reaction between Hydrogen and Sulphur. Part II.* (1) *Formation and Characteristics of the Unimolecular Layer of Hydrogen Sulphide on the Glass Surface.* (2) *Independence of the Reaction of the Presence of Oxygen, Moisture, and Sulphur Dioxide.*

By ERNEST E. AYNSLEY and PERCY L. ROBINSON.

IN a preceding communication (this vol., p. 58) hydrogen and sulphur have been shown to combine in glass vessels, homogeneously, at a velocity proportional to the concentration of hydrogen and to the square root of that of the sulphur throughout the range 280—343° and 153—382 mm. pressure of hydrogen (measured at 15°). This has been repeatedly confirmed and found to hold also for pressures between 20 mm. and 686 mm. (measured at 15°) (Table I). The static method employed is capable, with these materials, of a precision rare in measurements of reaction velocities, and permits the reaction to be examined with hydrogen pressures as low as 1 mm. At low pressures, the measurements disclosed the unexpected fact that the surface of the reaction vessel becomes covered with a unimolecular layer of hydrogen sulphide formed heterogeneously thereon, and thereafter, ceases to exert further influence on the reaction. The experiments here described throw some light on the mode of formation of this film, and demonstrate the tenacity with which it adheres to the glass. It appears that hydrogen sulphide is only slightly adsorbed by glass when not actually formed on the surface, but that such adsorption does not contribute appreciably to the formation of the unimolecular film just mentioned.

TABLE I.

Sulphur concentration = 0·245 mg./c.c.; p = hydrogen pressure (mm. Hg), measured at 15°, v = velocity of H_2S formation, g./sec./c.c. of gaseous volume $\times 10^{10}$.

Temp.	p.	v.	$10^{14}v/p$.	Temp.	p.	v.	$10^{14}v/p$.	Temp.	p.	v.	$10^{14}v/p$.
301·0°	686	20·18	294	311·5°	382	22·70	594	322·0°	20	2·40	1200
301·0	382	11·50	301	311·5	20	1·14	570	343·0	686	256·80	3744
301·0	20	0·65	325	322·0	686	75·80	1105	343·0	382	150·20	3931
311·5	686	39·00	569	322·0	382	44·20	1157	343·0	20	7·70	3850

Results obtained by a dynamic method have been interpreted (Norrish and Rideal, J., 1923, **123**, 1689) as showing that oxygen has a complicated catalytic influence on the combination of hydrogen with sulphur, exerting a strong poisoning effect on the gaseous reaction at all temperatures. Our own experiments, however, leave no doubt that, under static conditions at least, the established characteristics of the homogeneous reaction remain unaltered by oxygen. Actually, the oxygen is quickly converted into sulphur dioxide, and, provided the glass surface presented be small, this gas remains in the system unchanged. In the presence, however, of a considerable surface, it reacts slowly and heterogeneously with hydrogen sulphide to form steam and sulphur. Furthermore, neither oxygen nor sulphur dioxide has a detectable effect on the velocity of the reactions producing hydrogen sulphide at temperatures about 340°, and steam is also without appreciable influence.

I. *The Unimolecular Layer of Hydrogen Sulphide on the Glass Surface.*

The gas-distributing apparatus employed differed from that previously used by us (*loc. cit.*) only in having ground-glass instead of rubber joints for attaching the reaction bulbs, and a McLeod gauge in addition to one of the barometer type. The hydrogen was deoxygenated, washed, and dried exactly as before, and the sulphur was of similar quality to that already employed. The pressures of hydrogen in the bulbs were measured with an accuracy of $\pm 0·01$ mm.; the sulphur was weighed on a microbalance with a precision of $\pm 0·005$ mg. The hydrogen sulphide present after the reaction was estimated with a certainty of $\pm 0·02$ mg., for which purpose 0·001N-iodine solution was employed with a correspondingly dilute thiosulphate solution for

back titration, both solutions being freshly prepared and standardised against potassium dichromate at each estimation.

Hydrogen pressure = 1·35 mm. measured at 15°. Sulphur concentration = 0·245 mg./c.c.

Velocity of H_2S formation, g./sec./c.c. of gaseous vol. × 10^{10}.

Temp.	Found.	Calc.
343°	0·66	0·53

The data (above) show that at pressures of the order of 1 mm. the hydrogen sulphide formed exceeds the amount calculated from the velocity established for the homogeneous reaction occurring between 20 and 686 mm. of hydrogen. This increase arose from a second distinct reaction which was proved, quantitatively, to be heterogeneous, since it increased by no less than 400% in packed vessels. Quantitative response to precisely known changes in the area of

TABLE II.

The new reaction in relation to the area of glass surface.

Reaction temp. = 343°. Hydrogen press. = 1·26 mm. at 15°. Sulphur conc. = 0·245 mg./c.c.

Area of glass surface, sq. cm.	Yield of H_2S in the first hour from total surface, g. × 10^6.	Yield of H_2S/hour/sq. cm. of surface × 10^{10}.
1655	71	429
936	43	459
180	9	500

glass surface, brought about by packing the bulbs with clean-cut, quill tubing, was next observed. The results (Table II) were obtained after the first hour of heating, the yields being from the new surface reaction alone, which were computed by deducting from the total amount of hydrogen sulphide produced that formed in the homogeneous reaction. It is clear that the velocity of the new reaction is initially directly proportional to the surface area. It was, however, independent of sulphur concentration over the considerable range studied, as shown by the data in Table III.

TABLE III.

Hydrogen press. = 1·26 mm at 15°. Vol. of reaction vessel = 290 c.c Reaction temp. = 343°.
Period of heating = 1 hr. Total area of glass = 936 sq. cm.

Weight of sulphur, mg.	Total yield of H_2S in first hour, g. × 10^6.	H_2S from homogeneous reaction, g /hr. × 10^6 (calc.).	H_2S from surface reaction, g./hr. × 10^6.
71	95	52	43
1·72	48	8	40
1·28	53	7	46

A notable feature of the reaction is the fact, brought out in Table IV, that the amount of hydrogen sulphide produced in the surface reaction ceases to increase after about the first hour.

TABLE IV.

Hydrogen press. = 1·26 mm at 15°. Total glass area = 936 sq. cm. Reaction temp. = 343°.

Time of heating, mins.	Total yield H_2S, g × 10^6.	H_2S from homogeneous reaction, g. × 10^6 (calc.).	H_2S from surface reaction, g. × 10^6.
15·	41	13	28
30	65	26	39
60	95	52	43
90	117	78	39
120	148	103	45

In this time an amount of hydrogen sulphide has been produced which is of the same order as that required to cover the whole of the glass surface with a film of gas one molecule thick. This conclusion has been reached from the following considerations :

Weight of film = 0·042 mg. Area of glass surface = 936 sq. cm. Then, if the hydrogen sulphide molecule has a mean cross-section of $0·773 × 10^{-15}$ cm.² (Rankine and Smith, *Phil. Mag.*, 1921, **42**, 601, 615),

$$\text{area of film one molecule thick} = \frac{42 × 10^{-6} × 6·1 × 10^{23} × 0·773 × 10^{-15}}{34} = 582 \text{ sq. cm.}$$

From this result it would appear that the film of hydrogen sulphide is 582/936, *i.e.*, 0·6 molecule thick. This value lies near to unity, and since there is nothing inherent in the method which

prevents it from having any value whatsoever, it may be taken as signifying that the film is unimolecular.

The characteristics of this newly observed heterogeneous reaction lead to certain deductions of interest. In the first place, as it is independent of the sulphur concentration, whilst the gaseous reaction is related thereto, the two processes necessarily proceed independently, and furthermore, the hydrogen sulphide formed in the gaseous phase is evidently not adsorbed at the surface in a way which interferes with the mechanism of the surface reaction. Since the latter is independent of the concentration of sulphur vapour and related to the surface area, it is undoubtedly between sulphur adsorbed on the surface and molecules of hydrogen striking the surface. The reaction presents a similarity to the one we (*loc. cit.*) have already shown to occur between a surface of liquid sulphur and hydrogen, but differs in its complete cessation when sufficient hydrogen sulphide has been produced to form a unimolecular film. At a surface of liquid sulphur there is no such inhibition of the reaction by its products, and hydrogen sulphide continues to be formed so long as liquid sulphur is available. The difference appears to be due to the strong adsorption of hydrogen sulphide at a glass surface on which it is formed, and, on the other hand, to its relative freedom to leave a surface of liquid sulphur by evaporation into the gaseous phase. There is, however, probably no fundamental difference between the two reactions; otherwise it would be difficult satisfactorily to account for the fact that the ratio of effective collisions of hydrogen molecules on the virgin film to the same area of liquid sulphur is practically unity under similar conditions.
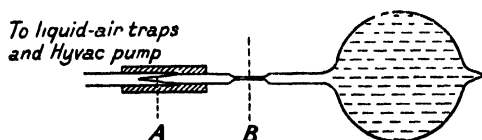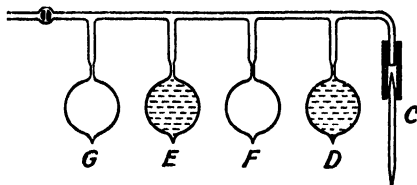
FIG. 1.

FIG. 2.

To liquid-air traps and Hyvac pump

A   B

G   E   F   D   C

Since the adsorbed sulphur gives rise to only a single layer of hydrogen sulphide molecules, it seems certain that the glass surface is originally covered by a sulphur film at least one molecule thick. As, however, the hydrogen sulphide molecules are retained on formation, it seems improbable that the foundation layer of sulphur is more than a single molecule thick. That sulphur in the presence of hydrogen should completely cover the surface is in keeping with the fact that the latter is not adsorbed and does not compete for the surface. The molecules in the sulphur film may be polyatomic but are more probably diatomic at the temperatures under consideration, in which case the residual fragment of the molecule, after the abstraction of a single atom from it in the course of the reaction, may either evaporate and leave its place to be occupied by the newly-formed hydrogen sulphide molecule, or remain as a foundation upon which the hydrogen sulphide rests. An alternative view is that the sulphur atoms, present in small quantity in the vapour, are preferentially adsorbed by the glass surface (compare Langmuir's study of the oxygen films formed on a hot tungsten surface), in which case there is no residual sulphur after combination. In either event, the adsorbed sulphur is probably specifically oriented in respect to the surface and, since the reactions on the film and on liquid sulphur appear to be identical, support is lent to the idea that the surface of liquid sulphur is composed of specifically disposed molecules.

That the unimolecular layer of hydrogen sulphide is strongly held by the surface on which it is formed, was demonstrated by carrying out the synthesis in a packed bulb of the form shown in Fig. 1, and afterwards breaking the tip A under a vacuum in a heavy rubber tube and rapidly evacuating the bulb through liquid-air and other protective traps by means of a Hyvac pump, until a good vacuum was obtained and, finally, sealing off the bulb at B. In these circumstances, an amount of hydrogen sulphide was retained in the bulb which was 70% of that required to cover the available surface with a unimolecular layer. It was clearly desirable to know whether hydrogen sulphide as such was adsorbed to any extent by a clean glass surface,

A A

and as this normal adsorption did not appear to have been previously investigated, presumably on account of manometry difficulties, some measurements were made at 0·25 mm. pressure. For this purpose, pure, dry hydrogen sulphide at atmospheric pressure in the tube *C*, Fig. 2, was allowed to expand in an evacuated system consisting of two packed bulbs, *D* and *E*, and two unpacked bulbs, *F* and *G*. After being sealed off, the packed bulbs contained more hydrogen sulphide per unit of available volume than the unpacked, the excess being, however, only 20% of the amount required to cover the surface with a unimolecular layer. In similar circumstances, sulphur dioxide showed no excess in the packed bulbs and is presumably not adsorbed under these conditions.

The unimolecular layer which has been observed in this study of the hydrogen–sulphur reaction effectively prevents the surface from promoting further action between hydrogen and sulphur with pressures of the former up to 686 mm. (measured at 15°). The actual amount of hydrogen sulphide involved in the formation of the unimolecular layer is small even in packed bulbs, and undetectable except when the total yield is small. Thus the composite reaction at about 343° in the absence of liquid sulphur naturally appears to be homogeneous with hydrogen pressures from about 20 mm. upwards, exactly as we found it.

Unimolecular gas films on solids were first described by Langmuir (*J. Amer. Chem. Soc.*, 1915, **37**, 1162), who showed that such an oxygen film changed the character of a hot tungsten surface by increasing its ability to hold cæsium atoms and completely removing its power to dissociate hydrogen molecules. Subsequent workers have investigated adsorption films on glass : Carver (*ibid.*, 1923, **45**, 63) found that toluene vapour most probably gives a unimolecular film, and a similar result has since been obtained by Crespí (*Anal. Soc. Fís. Quím.*, 1932, **30**, 520) for nitrous oxide; whilst, on the other hand, Evans and George (*Proc. Roy. Soc.*, 1923, **103**, 190), who employed a number of different gases, found the layers to be multimolecular, *viz.*, 39·9 molecules with ammonia and 3·5 with acetylene. Water vapour has also been described as giving a multimolecular layer. The question of the formation of unimolecular films in the case of glass was thus an open one, and consequently special interest attaches to the film of hydrogen sulphide now described, because it is not only definitely unimolecular, but has in addition specific chemical characteristics and, as does Langmuir's oxygen film on tungsten, profoundly alters the catalytic character of the surface which it covers.

II. *The Influence of Oxygen, Sulphur Dioxide, and Moisture on the Velocity of the Homogeneous Reaction between Hydrogen and Sulphur.*

Pyrex-glass bulbs containing appropriate quantities of sulphur were filled at known pressures with various mixtures of hydrogen and oxygen of definite composition. These mixtures were prepared by measuring the gases carefully, a McLeod gauge being employed for the lower range of oxygen pressures, and allowing them, before use, to mix thoroughly in a vessel attached to the all-glass distributing system. The amount of sulphur used, whilst sufficient to combine with the oxygen several times over, was always insufficient to leave liquid at the reaction temperatures, *viz.*, 290—343°. Both packed and unpacked bulbs were used. The reaction products were hydrogen sulphide and sulphur dioxide and, in addition, uncombined sulphur and hydrogen were present. The contents of the bulbs after reaction were treated with standard iodine in the manner already described (this vol., p. 58) and the resulting liquid was back-titrated with sodium thiosulphate to ascertain the amount of iodine reduced. The portion of the titre due to sulphur dioxide was found by filtering off the sulphur from the liquors after titration and estimating the sulphate present as barium sulphate, with parallel blanks on all the reagents employed. Oxidation with iodine, followed by filtration and precipitation with barium chloride, without reduction of the excess iodine with thiosulphate, gave identical sulphate results.

Separate experiments, which will be described elsewhere, showed that when mixtures of sulphur dioxide and hydrogen sulphide, at a total pressure up to approx. 45 mm. of the mixed gases, are treated with aqueous iodine, there is no perceptible reaction between the two gases. Hence the iodine titre is equivalent to the sulphur dioxide together with the hydrogen sulphide (Table V).

By varying the time of heating in different unpacked bulbs, it was shown that the oxidation of the sulphur takes place so rapidly that after a short heating the whole of the oxygen has been converted into sulphur dioxide, and subsequently the hydrogen–sulphur reaction proceeds at

TABLE V.

Reaction temp. = 322°. The figures in the table represent c.c. of 0·01N-iodine.

Determined.			Calculated.		
$H_2S + SO_2$.	SO_2, grav.	H_2S, by diff.	SO_2 = all O_2.	H_2S.	$H_2S + SO_2$.
86·6	64·8	21·8	63·2	21·4	84·6
84·3	62·9	21·4	62·5	21·1	83·6

precisely the velocity found when hydrogen and sulphur only are present (Table VI). Thus oxygen, up to about 7% by volume, and sulphur dioxide are without effect on the hydrogen–sulphur reaction. This result is in conflict with that of Norrish and Rideal (J., 1923, **123**, 1689), who found that oxygen exerts " a strong poisoning effect in the gaseous reaction between hydrogen and sulphur at all temperatures."

TABLE VI.

Volume of bulb = 223 c.c. Hydrogen press. = 384·6 mm. at 17°. Weight of sulphur present = 0·0546 g. Oxygen press. = 1·025 at 17°. Reaction temp. = 301°. The figures in the table represent c.c. of 0·001N-iodine.

Period of heating, mins.	$H_2S + SO_2$.	SO_2 = O_2 (calc.).	H_2S, by diff.	H_2S, calc. from velocity of reaction.
15	38·0	24·7	13·3	13·5
30	48·9	24·7	24·2	27·1
60	78·1	24·7	53·4	54·2
120	132·2	24·7	107·4	108·3
180	185·7	24·7	161·0	162·5

In one hour, in unpacked bulbs, there is a barely detectable interaction between sulphur dioxide and hydrogen sulphide, whereas in packed bulbs appreciable reaction takes place between the gases, resulting in the formation of sulphur and steam. With an area of glass surface of 1600 sq. cm., about 9% of the hydride–oxide mixture reacts in one hour at 343°. Evidently the velocity of the reaction is low, and if it is assumed to be proportional to the area of the surface, it should be just perceptible in our unpacked bulbs. Actually, it could just be detected, as may be seen in the higher portion of Curve A, Fig. 4, Part I (*loc. cit.*). The demonstration of the heterogeneous character of this reaction confirms the work of Taylor and Wesley (*J. Physical Chem.*, 1927, **31**, 216), who, using a dynamic method, drew the same conclusion. With certain of their higher concentrations, Norrish and Rideal found the total yield of hydrogen sulphide to fall to nearly zero, an effect which, in our opinion, may be more simply explained by reference to interaction between sulphur dioxide and the hydrogen sulphide than by assuming a negative catalysis of the synthesis.

The reaction $2H_2S + SO_2 = 2H_2O + 3S$ involves the formation of steam, which, in the limited quantities present, does not appear to affect the hydrogen–sulphur reaction. To confirm this view, specific experiments were made with hydrogen containing 2% by volume of water vapour, and velocities were obtained which were identical with those already found when hydrogen which had been previously carefully dried over phosphoric oxide was used (see below) :

Reaction temp. = 343°.

Treatment of hydrogen.	Velocity of H_2S formation, g./sec./c.c. of gaseous vol. $\times 10^{10}$.
Dried over P_2O_5	150·2
Containing 2% H_2O (by vol.)	150·1

SUMMARY.

1. The reaction between hydrogen and sulphur has been studied for the first time at pressures of the order of 1 mm., and it has been shown that (i) the characteristics of the homogeneous reaction previously described by us are maintained under these conditions; (ii) a heterogeneous reaction takes place at the surface of the glass but continues only until a unimolecular layer of hydrogen sulphide has been formed thereon. All the hydrogen sulphide formed is retained by this surface and the unimolecular layer has specific properties (cf. Langmuir's oxygen film on tungsten) and prevents further participation of the surface in the reaction.

2. The homogeneous combination of hydrogen and sulphur has been studied in the

presence of oxygen, sulphur dioxide, and moisture, and it has been shown that none of these gases has any effect on the velocity of the reaction.

78. *Solubilities of the Double Magnesium Nitrates of the Cerium Group.*

By J. NEWTON FRIEND and (in part) W. NORMAN WHEAT.

THE double nitrates of magnesium and the metals of the cerium group are frequently used in the separation of the latter by fractional crystallisation either from acid (Demarçay's method, *Compt. rend.*, 1896, **122**, 728; 1900, **130**, 1019) or neutral (Drossbach, *Ber.*, 1902, **35**, 3827) solution. Their general " ideal " formula is $3Mg(NO_3)_2,2M(NO_3)_3,24H_2O$, where M represents elements No. 57 to 62. Appreciable variation in composition occurs, however, if the mother-liquor does not contain the theoretical proportions of the constituent salts. All are hygroscopic and yield supersaturated solutions with ease. As the data concerning their relative solubilities in water are scanty, it seemed desirable to study them more closely.

Jantsch (*Z. anorg. Chem.*, 1912, **76**, 303) has given their solubilities (except for Il, No. 61) at 16° in nitric acid of *d* 1·325 and their congruent melting points. This high acid concentration was used because his supply of material was too small to admit of the determination of the solubility in pure water or dilute acid. Prandtl and Ducrue (*ibid.*, 1926, **150**, 105) determined the solubilities of the praseodymium and neodymium double salts in water at 15°, 30°, 50°, and 70°, and Friend (J., 1930, 1903) determined the solubility of the latter in water and in nitric acid solutions over the range 0° to 90°. Apart from these, no systematic data appear to have been published.

In the present research, the solubilities of the lanthanum and cerium salts have been determined for the first time, and further data have been obtained for the praseodymium salt.

The apparatus used has already been described (Friend, J., 1930, 1633).

At first, considerable difficulty was experienced in obtaining reproducible results. This was particularly so at the lower temperatures, and the solubility appeared to vary with the relative proportions of solution and undissolved salt in the saturation bottle. It was thought that this might be due to an initial selective dissolution of the components of the double salt so that true equilibrium between solution and crystals might not be easily attained, although the solutions in the saturation bottle were agitated at constant temperature for some 4—6 hours. An attempt was made to overcome this difficulty by preparing a more or less saturated solution at 90—100° and quickly cooling it to the required temperature in a thermostat; stirring for several hours after this was essential to remove supersaturation, to which these salts are prone. As obtained in this way, the results were more concordant but still not quite as good as one usually obtains with single salts.

Lanthanum Magnesium Nitrate, $3Mg(NO_3)_2,2La(NO_3)_3,24H_2O$.—The initial supply of lanthana was purchased from Messrs. Hilger; it was very free from other rare earths and contained only the merest trace of Pr_6O_{11}, which imparted a barely perceptible brown tint to it. The double salt was prepared by dissolving the requisite amounts of lanthana and B.P. magnesium oxide in dilute nitric acid, crystallising, and recrystallising from dilute acid.

Method of analysis. Determination of the two oxides was regarded as sufficient. Usually the crystals were dissolved in water and diluted to 250 c.c. The lanthana was estimated by precipitation from 50 c.c. with excess oxalic acid from hot solution and ignition to oxide; the precipitate was less granular than that of neodymium or praseodymium, and it was found

advisable to digest it on the water-bath for several hours and keep it over-night before attempting to filter it off. A further 50 c.c. were taken to dryness in a platinum dish, ignited to the mixed oxides, and magnesium oxide calculated by difference. A few analyses are as follow :

	1.	2.	3.	4.	5.	Calc.
La$_2$O$_3$ (%)	21·05	18·67	20·20	20·23	21·05	21·33
MgO (%)	8·03	7·34	7·77	8·07	7·66	7·92
Ratio La$_2$O$_3$/MgO	2·62	2·54	2·60	2·51	2·75	2·69

Even when well-developed crystals were chosen, their compositions showed considerable variation in the La$_2$O$_3$: MgO ratio according to the composition of the mother-liquor. It was important, therefore, to check the composition of every batch of crystals; this complicated the work, for, owing to the relatively limited supply of material and the high solubility of the salt, the residues had to be repeatedly worked up.

When only small batches of salt were available, the two oxides were estimated in the same sample by first igniting it to mixed oxides; these were subsequently dissolved in acid and the lanthana determined as before. The results were equally satisfactory, as the following data indicate :

La$_2$O$_3$ (direct), g.	0·2007	0·3189	0·3298	0·3791
La$_2$O$_3$ (after ignition), g.	0·2008	0·3184	0·3294	0·3801

This shows that if any compound is formed during ignition it is completely decomposed by subsequent treatment. As explained later, this method could not be adopted with the praseodymium and cerium salts.

Solubility. The solubilities, S, given below are expressed as g. of hydrated salt per 100 g. of solution ; they are also shown in the fig.

Temp.	18·6°	31·6°	46·8°	50·8°	61·4°	74·8°	113·5° *
S	62·19	63·96	68·57	70·17	73·05	77·43	100
Ratio La$_2$O$_3$/MgO	2·68	2·61	2·08	2·60	2·63	2·59	—

* Melting point (Jantsch, *loc. cit.*).

Praseodymium Magnesium Nitrate, 3Mg(NO$_3$)$_2$,2Pr(NO$_3$)$_3$,24H$_2$O.—This salt was prepared by dissolving the calculated quantities of Pr$_6$O$_{11}$ and magnesium oxide in dilute nitric acid and crystallising. The original supply of Pr$_6$O$_{11}$ was purchased from Messrs. Hilger and was very free from other rare earths. The oxide was dissolved in nitric acid, and the oxalate precipitated and ignited in order to remove traces of halide found to be present. The supply of crystals of double salt was seldom sufficient for more than one solubility determination ; it was necessary, therefore, repeatedly to work up the residues and prepare fresh batches. Moreover, it was necessary to analyse each batch, since the crystals showed analogous variations to those of the lanthanum salt (see analyses below).

Method of analysis. Determination of the two oxides was regarded as sufficient. The former was estimated by precipitation as oxalate, ignition in a platinum crucible and weighing as Pr$_6$O$_{11}$ (Brinton and Pagel, *J. Amer. Chem. Soc.*, 1923, **45**, 1460), the precautions already detailed (Friend, J., 1932, 2410) being observed. Duplicate experiments showed satisfactory concordance, as the following pairs indicate : Pr$_6$O$_{11}$, g. : 0·2548, 0·2538; 0·2668, 0·2676; 0·3220, 0·3226.

When heated with certain oxides, such as lanthana and ferric oxide, the state of oxidation of the praseodymium varies between the limits Pr$_2$O$_3$ and PrO$_2$ according to circumstances (Prandtl and Huttner, *Z. anorg. Chem.*, 1925, **149**, 235) ; but the presence of magnesium oxide is stated to have no influence, the oxide being Pr$_6$O$_{11}$. It was thought, therefore, that the method of determining magnesium oxide by difference, as before, would prove satisfactory ; but the observed ratio Pr$_6$O$_{11}$: MgO was always lower than expected; this, coupled with the fact that there was usually a difficulty in obtaining a constant weight on ignition, suggested that Pr$_6$O$_{11}$ is not so inert towards magnesium oxide as Prandtl believed.

To test this, solutions of the two nitrates of known concentration were mixed, evaporated and ignited, with the following results :

Pr$_6$O$_{11}$ taken, g.	MgO taken, g.	Total taken, g.	Ratio Pr$_6$O$_{11}$: MgO.	Obs. wt. of mixed oxides, g.	Increase in wt. of Pr$_6$O$_{11}$, %.
0·4030	0·1492	0·5522	2·70 : 1	0·5573	1·29
0·2538	0·1315	0·3853	1·93 : 1	0·3886	1·30
0·2548	0·1687	0·4235	1·51 : 1	0·4268	1·30

For complete oxidation of Pr_6O_{11} to PrO_2 the percentage increase in weight is 1·57; under the conditions of the experiments, therefore, more than 80% of the Pr_6O_{11} had been converted into PrO_2. In calculating the weight of magnesium oxide by difference from the mixed oxides this correction must be applied. The result is sufficiently accurate for present purposes, as the solubility data are based on the quantity of praseodymium present in solution. Typical analyses of different batches of the double salt are as follow:

	1.	2.	3.	4.	Calc.
Pr_6O_{11} (%)	21·57	21·24	21·02	21·35	22·24
MgO (%) (corr.)	7·81	7·97	7·37	7·48	7·90
Ratio (corrected)	2·76	2·67	2·85	2·86	2·82

Solubility. The following solubilities, *S*, are expressed as before; they are also shown in the fig. The data in parentheses are those of Prandtl and Ducrue (*loc. cit.*); the agreement is good.

Temp.	15·0°	17·8°	30·0°	37·4°	50·0°	61·8°	70·0°	74·6°	111·2° *
S	(63·0)	63·1	(66·4)	67·74	(71·0)	74·25	(77·5)	78·39	100

* Melting point (Jantsch, *loc. cit.*).

Cerium Magnesium Nitrate, $3Mg(NO_3)_2,2Ce(NO_3)_3,24H_2O$ (with W. N. WHEAT).—In the preparation of this salt, Kahlbaum's cerous nitrate was used.
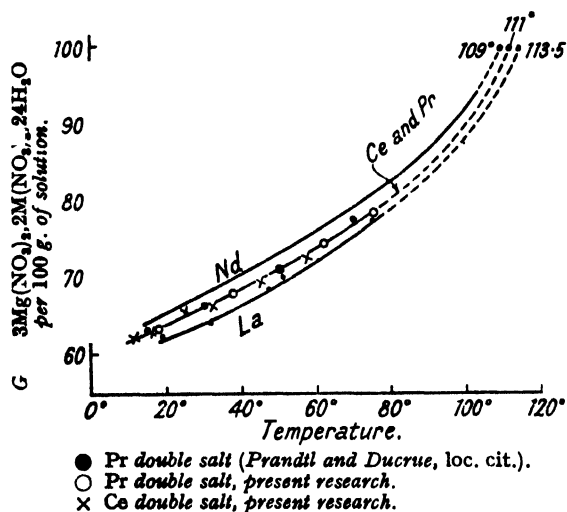
Method of analysis. Determination of CeO_2 and magnesium oxide was regarded as sufficient. The former was estimated by precipitation as oxalate and ignition; the latter was determined by difference from the mixed oxides from a second aliquot portion. That this method yields fairly accurate results was proved by separate determinations of the magnesium as phosphate. The following results are typical:

● Pr *double salt (Prandtl and Ducrue,* loc. cit.).
○ Pr *double salt, present research.*
× Ce *double salt, present research.*

MgO (by difference)	0·0744	0·0823
MgO (as phosphate)	0·0753	0·0814

It is evident that the presence of magnesium oxide does not appreciably alter the state of oxidation of the cerium. It was not practicable to determine the ceric oxide and magnesium oxide from the same sample by difference, owing to the difficulty of dissolving the former after the first ignition to mixed oxides.

The compositions of the crystals of different batches of double salt showed variations similar to those of the preceding double salts. The following analyses are illustrative:

	1.	2.	3.	Calc.
CeO_2 (%)	21·45	21·39	22·44	22·51
MgO (%)	8·24	8·61	7·90	7·91
Ratio CeO_2/MgO	2·004	2·485	2·841	2·846

Solubility. The following solubilities, *S*, are expressed as before and are also shown in the fig.

Temp.	11°	16°	24·6°	31·8°	42·2°	57·0°	111·5° *
S	61·98	62·89	65·63	66·20	69·26	72·78	100
Ratio CeO_2/MgO	2·84	2·78	2·87	—	—	2·77	—

* Melting point (Jantsch, *loc. cit.*).

The solubility curves of the praseodymium and the cerium salt are very similar, and lie between those of the lanthanum and the neodymium salt. In concentrated acid solution, however, Jantsch found the cerium salt to be less soluble than the lanthanum salt. Possibly for this reason, it appears to be customary to remove cerium chemically from rare-earth mixtures prior to fractional crystallisation of the double nitrates. The results of the present research explain the observation of Feit and Przibylla (*Z. anorg. Chem.*, 1905, **43**, 205) that it may be an ad-

vantage to retain the cerium, or even to add more of it, in order to facilitate the separation of praseodymium along with it. A preliminary set of fractionations based on this principle gave encouraging results. To 250 g. of a mixture of praseodymium and neodymium double magnesium nitrates, at which the ratio Pr : Nd was about 15 : 85, approx. 50 g. of the cerium double salt were added. On fractionation the praseodymium salt rapidly collected along with the cerium salt in the head fractions.

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79. *The Structure of Cæsium Cobalt Chloride* (Cs₃CoCl₅).

By H. M. POWELL and A. F. WELLS.

ALTHOUGH a co-ordination number of 5 seems certainly to exist in some molecules, *e.g.*, those of phosphorus pentafluoride and iron pentacarbonyl, in general it is not to be expected. The avoidance of odd co-ordination numbers by heavy-metal atoms, even if this requires otherwise unusual effective atomic numbers in the molecule, has been demonstrated by Menzies (J., 1934, 1755). Stable complex ions AX_3 and AX_4 are well known, but if the co-ordination number exceeds 4, the next stable group is AX_6. There are, however, compounds of the type M_nRCl_5 which might appear to contain an RCl_5 group. Most of these are monohydrated, *e.g.*, K_2FeCl_5,H_2O, and it may be reasonably supposed that they contain the group $[RCl_5,H_2O]$, R having co-ordination number 6. A few, however, are anhydrous, and it appeared to be of interest to investigate the structure of such a compound.

Cæsium cobalt chloride, Cs_3CoCl_5, was selected for this purpose; its composition was established by Campbell (*Amer. J. Sci.*, 1894, **48**, 419), and according to microscopic examination by Vermande (*Pharm. Weekblad*, 1918, **55**, 1117), it crystallises in the tetragonal system.

EXPERIMENTAL.

Our material was prepared by crystallisation of an aqueous solution of cobalt chloride and excess of cæsium chloride. Deep blue tetragonal crystals Cs_3CoCl_5 were obtained, which on recrystallisation from water gave similarly coloured orthorhombic Cs_2CoCl_4. Analysis of the former substance was made on material which was shown microscopically to be free from included Cs_2CoCl_4 (Found : Co, as pyrophosphate, 9·51; Cl, as AgCl, 27·87. Calc. for Cs_3CoCl_5 : Co, 9·28; Cl, 27·93%. Calc. for Cs_3CoCl_5,H_2O : Co, 9·03; Cl, 27·16%). There was no appreciable loss of weight on heating the substance to 140°, and the X-ray and density measurements support the anhydrous formula.

Crystallographic Examination.—The crystals (Fig. 1) were found by measurement on a two-circle goniometer to be tetragonal. The lettering of the figure corresponds to indices according to the Barker system. For X-ray purposes, different axes and indices given by the transformation below are required :

FIG. 1.

Barker	a(100)	c(001)	r(101)	o(111)	cr = 48° 15'
X-Ray	110	001	112	⁻101	

Optically the crystals were uniaxial with weak positive double refraction. They showed no pyroelectric effect by the liquid-air method. The density was found by pyknometer to be 3·39 g./c.c. at 20°.

A complete series of 15° oscillation photographs about the *a* and *c* axes was made with copper radiation, and comparison spacing photographs with gypsum gave the cell dimensions $a = 9·18$, $c = 14·47$ Å.; $c : a = 1·576$ (calc., goniometric, 1·584). The number of molecules per unit cell is thus $3·95 \approx 4$. The oscillation photographs, indexed by the chart method, show that the space group is *I 4cm* or *I 4/mcm* (C_{4v}^{10} or D_{4h}^{18}), and from the absence of any evidence of polarity, the correct group is taken to be the latter. A preliminary determination of the
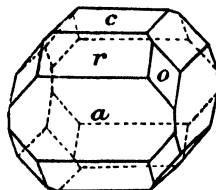
distribution of the atoms in the cell was made from consideration of the space group symmetry and some intensity comparisons. The possible equivalent positions are, in Wyckoff's notation ("Analytical Expression," 2nd. Edn.), four 4-fold a, b, c, d, and one 8-fold e without freedom, three 8-fold f, g, h, and two 16-fold i, j, with one degree of freedom, two 16-fold k, l, with two degrees of freedom, and one 32-fold with three degrees of freedom. In order to place 12Cs, 4Co, and 20Cl in the unit cell one 4-fold position must be assigned to each type of atom, and the possible distributions are 12Cs (8 + 4), 4Co (4), 20Cl (16 + 4), or (8 + 8 + 4). With three of the positions a, b, c, d, occupied, e and f become impossible for 8Cs or 8Cl, since there is now insufficient space to contain these atoms. The intensity calculated for the reflexion (400) is independent of the distribution of atoms among a, b, c, d, and, the observed intensity being nil, shows that 8Cs cannot be in either of the positions e and f or in g whatever the position of the remaining 16Cl. 8Cs must therefore be in h with fixed c axis co-ordinates, and it now becomes possible to determine the position occupied by 16Cl. The intensities for reflexions (00l) are such that there must be atoms in planes parallel to (001) other than those at heights 0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ along the c axis. Since all the atoms placed so far have fixed c co-ordinates 0, $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$, positions e, h, i, j, and k for chlorine are excluded. We therefore obtain the distribution 8Cs (h), u, $u + \frac{1}{2}$, $\frac{1}{2}$, etc., 16Cl (l), u', $u' + \frac{1}{2}$, v, etc., with 4Co, 4Cs, and 4Cl in some arrangement of a, b, c, d; $a = 000, 00\frac{1}{2}, \frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{1}{4}0, b = 0\frac{1}{2}0, \frac{1}{2}00, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, c = 00\frac{1}{4}, 00\frac{3}{4}, \frac{1}{4}\frac{1}{4}\frac{3}{4}, \frac{1}{4}\frac{1}{4}\frac{1}{4}, d = 0\frac{1}{2}\frac{1}{4}, \frac{1}{2}0\frac{1}{4}, 0\frac{1}{2}\frac{3}{4}, \frac{1}{2}0\frac{3}{4}$. The possible distributions among a, b, c, d, fall into six groups as far as their effect on the intensities of reflexions (00l) is concerned, and of these six, five are incompatible with observation for any value of the parameter v. Agreement is obtained with 4Cs in a or b, 4Co in a or b, 4Cl in c or d, and a chlorine parameter $v = \frac{1}{12}$ or $\frac{11}{13}$. The intensities calculated for (h00), which are the same for all combinations of a, b, c, d, allow a preliminary limitation of u and u' to the regions u or $(\frac{1}{2} - u) = 0\cdot13 - 0\cdot19$, u' or $(\frac{1}{2} - u') = 0\cdot11 - 0\cdot22$. There are only two essentially different ways of combining the alternative values for u, u', and v, and one of these,

TABLE I.

(Visually estimated intensities are in decreasing order vs, s, ms, m, w, vw.)

Indices.	Calc. $\sqrt{I}$	Obs. I.	Indices.	Calc. $\sqrt{I}$	Obs. I.	Indices.	Calc. $\sqrt{I}$	Obs. I.	Indices.	Calc. $\sqrt{I}$	Obs. I.
200	110	w	206	451	s	554	35	nil	181	81	vw
400	30	nil	208	110	w	556	80	nil	183	201	m
600	580	vs	2010	210	m	572	64	vw	185	93	w
800	67	nil	2012	30	nil	352	70	w	581	82	w
1000	35	nil	2014	146	m	354	196	m	583	213	m
002	120	w	402	309	ms	356	93	nil	585	79	w
004	870	vs	404	166	m	372	20	nil	347	21	nil
006	350	s−	406	398	s	374	134	w	222	193	m
008	440	vs	408	113	w	376	146	w+	224	627	vs
0010	20	nil	4010	152	m−	392	154	m	226	94	vw
0012	430	s−	4012	8	nil	394	64	w+	228	283	ms
0014	10	nil	602	40	nil	396	268	m+	2210	79	vw
0016	262	m	604	352	ms	121	300	ms	2212	210	m−
110	40	nil	606	186	w	123	590	vs	242	138	vw
220	600	vs	608	290	ms	125	227	m+	244	339	ms+
330	390	vs	6010	30	nil	127	162	w+	246	55	nil
440	370	vs	6012	371	vs	129	270	ms	248	222	ms
550	29 ·	nil	802	190	w	321	16	nil	442	156	m−
660	370	s	804	55	nil	323	45	vw	444	236	m+
770	38	nil	806	166	w	521	136	w	446	16	nil
310	540	vs	808	52	nil	523	305	ms	448	206	ms
350	230	m	8010	183	m	525	134	w+	622	238	m
370	245	m	112	184	m−	527	116	w	624	93	w
390	150	w	114	166	w+	721	118	w	626	280	ms−
190	172	w+	116	197	m	723	192	m	628	72	nil
570	14	nil	132	110	w	725	118	w	642	182	m
590	170	w+	134	356	s−	141	200	m	644	96	vw
240	430	vs	136	150	w+	143	366	s	646	288	ms
260	40	nil	138	222	m	145	190	m	648	97	w
280	180	m−	332	270	s	147	148	m	662	34	w
2100	222	m−	334	114	w	149	208	m	664	272	ms
460	0	nil	336	512	vs	541	124	m	666	138	w
480	165	w	338	77	w	543	251	m+	824	183	w+
4100	230	m	3310	172	w	545	123	w	844	182	m
202	566	s	3312	187	w	547	127	w	846	70	vw
204	215	m	552	78	vw	563	41	vw			

which would bring cæsium and chlorine atoms to within 2·7 Å. or less, is clearly impossible. The arrangement selected to represent the structure has $v = \frac{11}{12}$, $u = 0.13 - 0.19$, $u' = 0.11 - 0.22$. It then follows that 4Cl must be in c 00$\frac{1}{4}$, etc., 4Cs in a 000, etc., and 4Co in b 0$\frac{1}{2}$0, etc. This distribution may be obtained by consideration of ionic radii alone, and is supported by the probable atomic environments.

On the assumption of these co-ordinates, the parameters u and u' were determined simultaneously from the intensities of the reflexions $h00$, $hk0$, $hh0$, which are independent of v. The values could be easily limited to $u = 0.15 - 0.18$, $u' = 0.13 - 0.20$. With the aid of contour diagrams constructed to show the effect on intensities of simultaneous variation of u and u' in these limited regions, the values $u = 0.167$, $u' = 0.155$ were chosen to give the best agreement with observation. Intensities were compared by the formula

$$\sqrt{I} \propto \left(\frac{1 + \cos^2 2\theta}{2 \sin 2\theta}\right)^{\frac{1}{2}} \sum_n f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

In Table I are the values of $\sqrt{I}$ calculated as above. The f values of Pauling and Sherman (*Z. Krist.*, 1932, **81**, 1) were used, and where necessary the correction according to Cox and Shaw (*Proc. Roy. Soc.*, 1930, *A*, **127**, 71) for spots not on the zero layer line has been applied to the calculated $\sqrt{I}$.

DISCUSSION.

A unit cell of the structure and the immediate environment of the atoms are illustrated by Figs. 2 and 3. The principal interatomic distances are given in Table II, in which structurally different cæsium and chlorine atoms are distinguished by Roman numerals.

TABLE II.

Atom.	Co-ordinates.	Neighbours.	Distance, Å.
Cs^I	000	8Cl^{II}	3·67
		2Cl^I	3·62
Cs^{II}	u, $u+\frac{1}{2}$, $\frac{1}{4}$	2Cl^I	3·42
		2Cl^{II}	3·39
		4Cl^{II}	3·85
Cl^I	00$\frac{1}{4}$	2Cs^I	3·67
		4Cs^{II}	3·42
Cl^{II}	u', $u'+\frac{1}{2}$, v	1Co	2·34
		2Cs^I	3·67
		1Cs^{II}	3·39
		2Cs^{II}	3·85
Co	0$\frac{1}{2}$0	4Cl^{II}	2·34

FIG. 2.

● = Cs, ○ = Cl, • = Co.

The distances are in accordance with accepted values. For Cs–Cl in 10 co-ordination, the distance calculated from Zachariasen's tables (*Z. Krist.*, 1931, **80**, 137) is 3·64 Å., in good agreement with the Cs^I–Cl values. For eight neighbours Cs^{II}–Cl would be 3·58,

FIG. 3.

10Cl around Cs^I 8Cl around Cs^{II} 6Cs around Cl^I
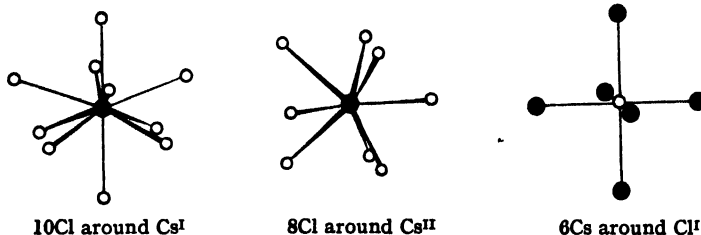
but the arrangement of chlorine around Cs^{II} is such that some variation in the distances is to be expected. In particular, it may be seen from the figures that four chlorine atoms which belong to CoCl₄ groups are pulled away on one side to 3·85 Å. On the same side also there is a cæsium ion at 4·32 Å., closer than the other cæsium neighbours at 4·84 Å., and these two influences account for the compression to *ca.* 3·4 Å. of the four Cs–Cl distances
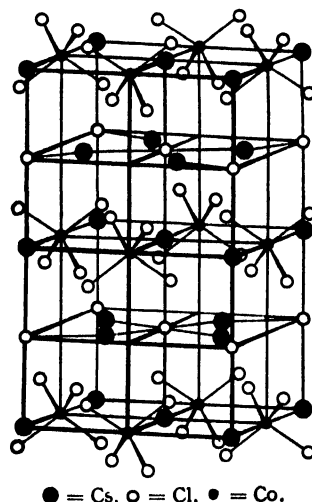
on the other side. The distance 2·34 for Co–Cl is what would be expected. From the co-valent radii (Sidgwick, " The Covalent Link ") the value is 2·22, or, from the crystal structure of cobalt chloride (Ferrari, *Atti R. Accad. Lincei*, 1927, **6**, 56; Grimes and Santos, *Z. Krist.*, 1934, **88**, 136) after allowance for co-ordination number, 2·42 Å.

Space-group considerations alone show that one of the four chlorine atoms per chemical molecule is different from the other four in relation to the cobalt. The detailed investigation reveals the presence of $CoCl_4$ groups in approximately regular tetrahedral configuration. The fifth chlorine stands apart as a Cl^{1-} ion far removed from the cobalt atom, and the compound should therefore be formulated $Cs_3^{1+}[CoCl_4]^{2-}Cl^{1-}$. It is analogous to $(NH_4)_3^{1+}[ZrF_6]^{2-}F^{1-}$ (Hassel and Mark, *Z. Physik*, 1924, **27**, 89).

Our results show how it is possible for a compound to simulate in chemical formula an RX_5 complex without necessarily containing a group of this unusual co-ordination number. It is difficult to predict when compounds of this type should be formed, but some light is thrown on this by the analogous *rubidium* compound. It was found possible to obtain blue tetragonal crystals of this compound (Found : Cl, 36·45. Rb_3CoCl_5 requires Cl, 36·0%) from a hot solution of the mixed chlorides, but it is very unstable, rapidly decomposing at the ordinary temperature either in or out of its solution. A fragment, which proved to be not altogether a single crystal, was treated to remove solution as completely as possible, and a 5° oscillation photograph taken about the [110] axis with a very short exposure. The results indicate a tetragonal cell, $a = 8·7$, $c = 14·0$ Å., and the substance is presumably isomorphous with the cæsium compound. The tendency for $M_3[CoCl_4]Cl$ to decompose into MCl and other products will be greater the higher the lattice energy of MCl. The stability of the compound therefore decreases with decreasing atomic number of the alkali metal M, in agreement with these observations, and corresponding potassium and sodium compounds will probably not exist.

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80. *The Reaction between Hydrogen Peroxide and Cerous Hydroxide.*

By A. LAWSON and E. W. BALSON.

IT is known (Pissarjewsky, *Z. anorg. Chem.*, 1902, **31**, 359) that hydrogen peroxide reacts quantitatively with excess of cerous hydroxide in suspension to give a precipitate of ceric hydroperoxide $Ce(OH)_3O·OH$, but the quantitative determination of the latter (Wieland and Rosenfeld, *Annalen*, 1930, **477**, 72) has caused considerable difficulty. From the work of Schwartz and Giese (*Z. anorg. Chem.*, 1928, **176**, 217), it appeared that the determination might be made by measurement of the oxygen evolved on adding acidified potassium permanganate solution ; also, Macrae (*J. Biol. Chem.*, 1933, **27**, 1248) dissolved the hydroperoxide in acetic acid and titrated the resulting solution iodometrically either directly or after decomposition of the peroxide with catalase (Macrae and Wieland, *Annalen*, 1930, **483**, 229). Tests with known small amounts of hydrogen peroxide, however, gave low results by the above methods, so we re-examined the reaction.

The addition of hydrogen peroxide to a suspension of cerous hydroxide at p_H 5·8—9·0 gives, almost immediately, a bright yellow colour, the peroxide being rapidly absorbed. The mixture does not take up or evolve appreciable amounts of oxygen over a period of 10 hours. After 24 hours, however, a slight evolution of oxygen takes place. On treatment with dilute sulphuric acid, a freshly prepared mixture becomes colourless, but a mixture which has been kept for some time gives a yellow solution ; oxygen is evolved in both cases.

On acidification of the mixture, peroxidic oxygen and ceric salt react according to the equation

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + O_2 + H_2SO_4 \quad . \quad . \quad . \quad . \quad (1)$$
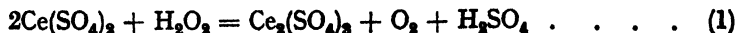
and, unless the two reactants happen to be present in this proportion, one or the other remains in solution. From measurement of the oxygen evolved and determination of

excess peroxide or ceric salt, it was possible to calculate the amounts of each of the latter present in the suspension, and it was found that, if $[H_2O_2]_0$ represents the amount of hydrogen peroxide added originally, then with increase of time : (i) the oxygen evolved rises to a maximum corresponding to $\frac{1}{2}[H_2O_2]_0$ and then falls; (ii) the amount of peroxide in the precipitate falls steadily from an initial value (determined by extrapolation) equivalent to $\frac{3}{2}[H_2O_2]_0$; (iii) the amount of ceric salt in the precipitate rises from an initial value equivalent to $\frac{2}{3}[H_2O_2]_0$; (iv) the peroxide content of the acidified solution gradually falls to zero, and ceric salt then appears and increases with increasing age of the suspension.

The above results are in agreement with the view that the following reactions take place in the precipitate :

$$2Ce(OH)_3 + 3H_2O_2 = 2Ce(OH)_3O{\cdot}OH + 2H_2O \quad \ldots \quad \ldots \quad (2)$$
$$Ce(OH)_3O{\cdot}OH + 2Ce(OH)_3 + H_2O = 3Ce(OH)_4 \quad \ldots \quad \ldots \quad (3)$$
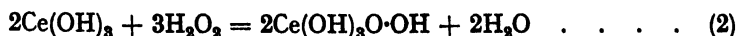
and on this basis the originally added hydrogen peroxide was always accounted for within an error of $\pm 3\%$.

The maximum in the oxygen evolution arises as follows. The relation between peroxidic oxygen and ceric salt in the precipitate is given by

$$2H^{\cdot} + 2Ce^{III} + H_2O_2 = 2Ce^{IV} + 2H_2O \quad \ldots \quad \ldots \quad \ldots \quad (4)$$
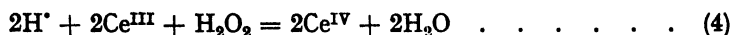
so, if 1 g.-mol. of hydrogen peroxide is added originally and a fraction x has been consumed in the oxidation of cerous salt, then $[H_2O_2] = 1 - x$ and $[Ce^{IV}] = 2x$. On acidification [equation (1)] the oxygen evolved is equivalent to $1 - x$ or to x g.-mols. according as ceric salt or peroxide is in excess, and when neither is in excess, $1 - x = x$, or $x = \frac{1}{2}$, so the oxygen evolution is equivalent to $\frac{1}{2}[H_2O_2]_0$.

The peroxide content of the precipitate can also be determined directly by measurement of the oxygen evolved on treatment with acidified potassium permanganate solution.

In order to follow the reaction during the first 9 mins., it was necessary to use a titrimetric method (see p. 364) instead of a gasometric method for determining the oxygen evolved on acidification, and this led to evidence for the formation of cerous hydroperoxide, $Ce(OH)_2O{\cdot}OH$, during these early stages. From equations (1) and (2), it is seen that the loss of peroxide in the precipitate should be equal to half the loss on acidification, but even after 9 mins. its value had not fallen to that required by (2) (loss of $\frac{1}{2}[H_2O_2]_0$) and extrapolation to zero time gave an initial peroxide value greater than $\frac{3}{2}[H_2O_2]_0$. It would appear, therefore, that cerous hydroperoxide is first formed according to

$$Ce(OH)_3 + H_2O_2 = Ce(OH)_2O{\cdot}OH + H_2O \quad \ldots \quad \ldots \quad (5)$$
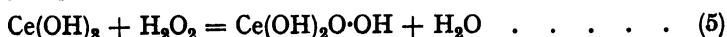
which causes no loss in available peroxide.

The course of the whole reaction would then be successively :

(a) (5)—fast, giving complete absorption of H_2O_2 within 3 mins.;
(b) $3Ce(OH)_2O{\cdot}OH + H_2O = 2Ce(OH)_3O{\cdot}OH + Ce(OH)_3$—fast, complete within 15 mins.;
(c) (3)—comparatively slow;

the net reaction being $2Ce(OH)_3 + H_2O_2 = 2Ce(OH)_4$.

It will be seen from the above that any method for the determination of hydrogen peroxide by cerous hydroxide at p_H 5·8—9·0 must take into account the fact that, although the whole of the oxidising power of the peroxide remains in the solution, it is distributed between ceric salt and a peroxide, the former continually increasing, and the latter correspondingly decreasing, with time.

Hydrogen peroxide may be determined by cerous hydroxide by measuring the oxygen evolved on acidification of the precipitate and the residual ceric salt or hydrogen peroxide present after acidification. Such a method yields good results for amounts of hydrogen peroxide of the order of 2—8 $\times$ 10^{-5} g.-mol. provided not more than about 6 hours elapse before acidification.

<div align="center">EXPERIMENTAL.</div>

Stability of the Cerous Hydroxide–Hydrogen Peroxide Complex.—To verify that no autoxidation of the cerous hydroxide suspension occurred, 2 c.c. each of 0·027N-cerous sulphate and 0·1M-borax

(p_H of mixture found to be 7·0) were placed in separate limbs of a modified Barcroft apparatus in a thermostat at 25°. They were then mixed, and during 24 hours no appreciable gas evolution or absorption took place. To verify that the peroxide precipitate underwent no loss in oxidising power, 2 c.c. of 0·027N-cerous sulphate and 0·8 c.c. of 0·1M-borax (p_H 6·2) were placed in one compartment of the Barcroft apparatus, and 1·0 c.c. of 0·048N-hydrogen peroxide in the other. Again, on mixing, no appreciable gas evolution or absorption took place within 10 hrs., but after 24 hrs., slight evolution of oxygen was observed.

Change of Composition of Complex with Time.—Determination of total peroxide content. (1) After short time intervals (before acidification). Expt. 1. 15 C.c. of 0·027N-cerous sulphate and 10 c.c. of 0·1M-borax were mixed, and 10 c.c. of 0·02475N-hydrogen peroxide added (p_H 6·4), the time being noted. All reagents were maintained at 25° before and after mixing. 5 C.c. portions (= 35·3 × 10^{-6} g.-mol. H_2O_2) were added to dilute sulphuric acid at noted times (with acetic acid the reaction, though taking place, was too slow for convenience; cf. Macrae and Wieland, *loc. cit.*), and the hydrogen peroxide in the resulting solution determined by adding a known excess of 0·1N-potassium permanganate and back titrating iodometrically. (This method is independent of any reaction between the permanganate and cerium, since they both react with iodide to give iodine.)

Expt. 2. The above procedure was repeated but with 25 c.c. of 0·0236M-hydrogen peroxide (p_H 6·2); 5 c.c. of the mixture therefore contained originally 59·0 × 10^{-6} g.-mol. H_2O_2.

TABLE I.

Expt.	Time, mins.	Free H_2O_2 after acidification.	Loss in H_2O_2 after acidification.	Loss in ppt.=½ × (loss on acidification).	H_2O_2 left in ppt.
1	0·75	21·8	13·5	6·7	28·5
	2·0	19·1	16·2	8·1	27·2
	3·0	17·4	17·9	8·9	26·3
	4·0	17·4	17·9	8·9	26·3
	5·0	16·3	19·0	9·5	25·8
	6·0	15·2	20·1	10·0	25·25
2	1·0	35·3	23·7	11·8	47·1
	2·0	32·8	26·2	13·1	45·9
	3·0	30·5	28·5	14·2	44·7
	4·0	28·0	31·0	15·5	43·5
	5·0	27·8	31·2	15·6	43·4
	6·0	26·7	32·2	16·1	42·9
	7·0	25·7	33·3	16·65	42·35
	8·0	25·0	34·0	17·0	42·0
	9·0	23·7	35·3	17·65	41·35

From the results in Table I (in which all weights are expressed as g.-mol. × 10^6) it will be seen that at the end of the run the peroxide content has not fallen to two-thirds of the original amount added.

(2) After long time intervals (before acidification). 25 C.c. each of 0·024M-hydrogen peroxide, 0·0135N-cerous sulphate, and 0·16M-borax (p_H 8·8) were mixed at 25°. From time to time, 5 c.c. portions were removed and placed in the Barcroft apparatus, 1 c.c. each of dilute sulphuric acid and 0·1N-permanganate being added together, and the oxygen evolution measured.

TABLE II.

Time, mins.	Total peroxide.	Time, mins.	Total peroxide.	Time, mins.	Total peroxide.	Time, mins.	Total peroxide.
16	25·4	51	21·4	129	17·8	256	16·8
34	22·4	86	18·8	160	17·5	405	15·7

From the results (Table II) it will be seen that the total peroxide decreases with time. Extrapolation to zero time gives a value for total peroxide equal to approximately two-thirds of the original amount added.

Determination of total peroxide and cerium. Expt. 1. 25 C.c. of 0·028M-hydrogen peroxide, 25 c.c. of 0·03N-cerous sulphate, and 20 c.c. of 0·1M-borax (p_H 6·1) were mixed. From time to time, 5 c.c. portions (equal to 50·8 × 10^{-6} g.-mol. H_2O_2 originally) were treated with dilute sulphuric acid and the oxygen evolution measured as above. The residual peroxide or ceric salt in the acidified solution was determined, the former titrimetrically as above, and the latter iodometrically.

Expt. 2. 25 C.c. of 0·0244M-hydrogen peroxide, 50 c.c. of 0·027N-cerous sulphate, and 20 c.c. of 0·1M-borax (p_H 6·3) were treated as in Expt. 1, 5 c.c. of solution being originally equiv-alent to 32·1 × 10^{-6} g.-mol. H$_2$O$_2$. The results are given in Table III, whence it will be seen that the oxygen evolution rises to a maximum and then falls, and that the maximum corresponds
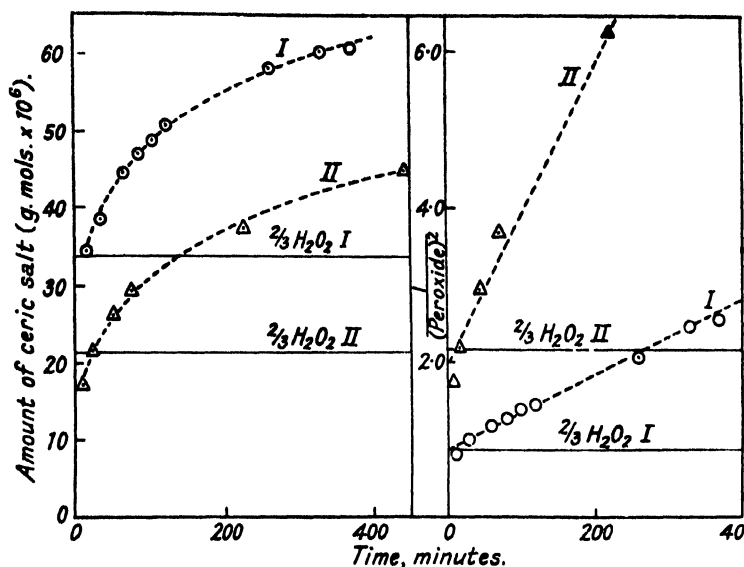
to half the peroxide originally added, *i.e.*, half of this has reacted to give ceric salt. Extrapola-tion to zero time gives an oxygen evolution approximately equal to that obtainable from Ce(OH)$_3$O·OH. Further, the total peroxide decreases and total ceric salt increases with time (see fig.). Extrapolation of both to zero time, the former by means of an empirical relation involving its square, gives values for ·OOH approximately equal to those obtainable from Ce(OH)$_3$O·OH.

TABLE III.

Expt.	Time, mins.	O$_2$ evoln.	H$_2$O$_2$ after acidification.	Ce^{IV} after acidification.	Total OOH.	Total Ce^{IV}.	$\dfrac{1}{[\cdot\text{OOH}]^2}$ *	Orig. H$_2$O$_2$ (calc.).	Error, %.
I	12	17·2	17·6	—	34·8	34·4	0·824	52·0	+2·4
	29	19·3	12·1	—	31·4	38·6	1·015	50·7	−0·2
	60	22·2	6·7	—	28·9	44·5	1·195	51·2	+0·8
	79	23·5	4·4	—	27·9	47·0	1·285	51·4	+1·2
	100	24·4	2·2	—	26·6	48·8	1·415	51·0	+0·4
	119	25·4	0·7	—	26·1	50·8	1·469	51·5	+1·4
	260	22·0	—	14·3	22·0	58·3	2·060	51·1	+0·6
	329	20·1	—	20·2	20·1	60·4	2·480	50·3	−1·0
	372	19·8	—	21·2	19·8	60·8	2·550	50·2	−1·2
	506	17·4	—	29·2	17·4	64·0	3·310	49·4	−2·8
II	7·5	8·6	15·4	—	24·0	17·2	1·740	32·6	+1·6
	20	10·9	10·3	—	21·2	21·7	2·22	32·0	−0·3
	49	13·1	5·3	—	18·4	26·2	2·95	31·5	−1·9
	73	14·7	1·9	—	16·5	29·4	3·67	31·2	−2·8
	224	12·7	—	12·1	12·6	37·4	6·30	31·3	−2·5
	446	10·5	—	24·1	10·5	45·1	9·02	33·0	+2·8
	1334	6·6	—	36·8	6·6	49·9	22·90	31·5	−1·9

* The values in this column are expressed in g.-mol. × 10^{-9}.

From results in Table III the original amount of peroxide (col. 9) present was calculated as indicated on p. 363, the maximum error being ± 3%.

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81. *Free Organic Radicals in the Gaseous State. Part IV. Synthesis of Antimony Cacodyl and Related Substances by the Use of Free Methyl and Free Ethyl.*

By F. A. Paneth and H. Loleit.

In previous communications (Part I, *Ber.*, 1929, **62**, 1335; Part II, *ibid.*, 1931, **64**, 2702; Part III, *ibid.*, p. 2708; see also *Z. Elektrochem.*, 1931, **37**, 577) the investigation of the reactions of free methyl and ethyl with zinc, antimony, and a few other elements served the purpose of proving the existence of the two radicals in the free state and of studying the mechanism of their reactions. The present contribution describes an attempt to utilise their activity for the systematic preparation of methyl and ethyl compounds of arsenic, antimony, and bismuth. Some of the products so obtained are new, attempts to synthesise them by the usual methods having failed.

It has already been pointed out that the impact of free methyl on antimony does not result in the formation of a homogeneous product; besides the colourless trimethylstibine, there is produced a substance of a strikingly red colour (in the solid state) which has now been shown, in agreement with a previous supposition (Parts I, p. 1341, and II, p. 2707), to be *bisdimethylantimony* ("antimony cacodyl"). Analogous experiments with arsenic showed that a still greater variety of products is formed : both radicals afford mono-, di-, and tri-alkyl derivatives. On the other hand, with bismuth only trialkyls have been identified. In all cases we examined the influence of temperature on the reacting mirror; for the synthesis of the highly alkylated and therefore easily volatile products, room temperature sufficed, but the yield of the less volatile di- and mono-alkyls is distinctly improved by heating the mirror. This device made it possible to obtain *bisdiethylantimony*.

I. *Reaction of Free Methyl and Free Ethyl with Arsenic.*—If at room temperature a mirror of arsenic is attacked by free methyl, bisdimethylarsenic (cacodyl; Bunsen, *Annalen*, 1842, **42**, 14) and trimethylarsine are formed, the former being the main product; free ethyl yields analogous compounds. Small quantities of less volatile yellow oils were also formed. Contact with air decomposes these compounds into white substances containing arsenic and having a disagreeable garlic-like odour.

The yields of the yellow oils were markedly increased by heating the arsenic mirrors. In an atmosphere of hydrogen, the methyl product polymerised slowly to a dark red solid, but the ethyl product remained unchanged. The arsenic content of the methyl compound agreed with that required for monomethylarsine. Substances of similar nature and composition have been described by various authors; although the recorded boiling points (see Experimental) vary considerably, it seems likely that all of them were cyclic pentamethylpentarsines, and that our substance, with a similar boiling point, is identical with them.

II. *Reaction of Free Methyl and Free Ethyl with Antimony.*—Cold and hot mirrors of antimony, treated with free methyl, formed trimethylstibine, together with a smaller quantity of a brilliantly red substance, which was shown by analysis and molecular-weight determination to be bisdimethylantimony, the analogue of Bunsen's cacodyl. Free ethyl gave very similar results, but the antimony mirror had to be heated for the production of the bisdiethylantimony; cold mirrors yielded almost exclusively triethylstibine. The former substance resembles its methyl analogue in colour but has a much lower melting point.

In both the methyl and the ethyl reactions, small quantities of black products were formed, the methyl compound being the more sensitive to air, but insufficient was obtained for detailed examination. A similar product was assumed by Schmidt (*Annalen*, 1920, **421**, 222) to be cyclic pentamethylpentastibine.

Since the dialkyl products were obtainable in fair quantity, we studied them in some detail. So far, antimony compounds of a similar structure have been known only in the aromatic series. Schmidt (*loc. cit.*) and Blicke, Oakdale, and Smith (*J. Amer. Chem. Soc.*, 1931, **53**, 1025) described a bisdiphenylantimony, but the existence of the corresponding

amyl compound (Berlé, *Annalen*, 1856, 97, 321) is doubted by Morgan and Davies (*Proc. Roy. Soc.*, 1926, *A*, 110, 523). Moreover, the latter authors failed to isolate bisdimethylantimony from the reaction of zinc with dimethylbromostibine, and we have confirmed their results, the failure obviously being due to the fact that bisdimethylantimony, although stable in a pure state, is decomposed at about 50° in the presence of zinc bromide. Our method avoids this difficulty, and although the yield is comparatively low (20—30 mg. per hour) the apparatus needs little supervision.

The most surprising property of bisdimethylantimony is its change of colour at the melting point: at 17·5° the bright red, needle-shaped crystals melt to a faintly yellow oil. At liquid-air temperature the colour is lighter than at room temperature, rather more orange; during slow warming, its colour deepens gradually and reaches its most intense tint immediately before melting. Its solutions in benzene, alcohol, ether, naphthalene, and camphor have a lighter colour than the oil. In water it sinks without dissolving or reacting; it dissolves in concentrated sulphuric acid with evolution of sulphur dioxide but without blackening.

Bisdimethylantimony reacts readily with mercury, so its vapour pressure was determined in a mercury-free manometer with the help of Bodenstein's silica spiral. The results are given in the following table, p being the pressure (in mm. of mercury) and t the temperature:

Vapour pressure of bisdimethylantimony.

$t.$	$p.$	$t.$	$p.$	$t.$	$p.$	$t.$	$p.$	$t.$	$p.$	$t.$	$p.$
64°	3·1	75·5°	5·9	86·5°	10·5	94·5°	14·5	100·5°	18·3	118°	40·5
69	4·6	76	6·4	89	10·9	97	16·9	102·5	21·1	130	62·7
75	6·3	86	10·1	92·5	14·2	99·5	17·6	107	26·1	140·5	91·2

Curve I in the fig. shows that, on plotting log p against the reciprocal of the absolute temperature, a straight line is obtained, whence we calculate the molecular heat of evaporation to be approximately 12 kg.-cals.
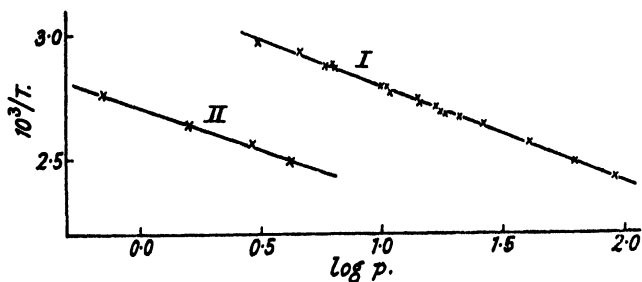
Determinations of the molecular weight in solutions in both benzene and camphor confirmed the bis-constitution, and showed that the compound is not appreciably dissociated; it seems, therefore, unlikely that the astonishingly strong colour of the solid is due to the formation of free radicals of dimethylantimony: special investigation will be necessary to explain the colour.* Spectroscopic examination shows two absorption bands in the green.

Bisdimethylantimony is very sensitive to oxygen: a quantity of about 100 mg., exposed to air, catches fire, and a smaller quantity fumes; in both cases a disagreeable garlic-like odour is perceptible. Benzene solutions also are oxidised in air, with formation of a white precipitate of dimethylantimonic acid (Morgan and Davies, *loc. cit.*); they also decolorise iodine and bromine solutions, and attempts to prepare definite products, by adding an equivalent quantity of one of the halogens and evaporating the solvent,

* We know of only one other instance of a strongly coloured organic substance which temporarily loses its colour when heated: the deep red base of diethylrhodamine gives a colourless solution in hot toluene, just as the red bisdimethylantimony becomes almost colourless in alcohol or benzene; but the explanation of the former colour change (Kuhn, *Naturwiss.*, 1932, 20, 622) cannot be applied to the case of the antimony compound.

afforded yellow oils with an antimony content corresponding to the formula $(CH_3)_2SbHal$. These partly solidified, and were quickly oxidised by air, developing white fumes. They were probably identical with the substances described by Morgan and Davies (*loc. cit.*), but their quantity was too small for their homogeneity to be ensured.

Bisdiethylantimony shows similar properties. At room temperature it is a yellow oil. When cooled to liquid-air temperature, it solidifies as an amorphous glassy mass, which, however, crystallises on slow heating; the colour is at first orange and becomes bright yellow near the melting point ($- 61°$). At higher temperatures the compound is somewhat less stable than the methyl analogue, decomposition beginning at $155°$. In spite of its lower m. p., it is much less volatile than the methyl compound; the vapour pressures are so small at the low temperatures to which the measurements necessarily have to be confined that the readings of the quartz spiral manometer cannot have a high degree of accuracy. From the results (see below, and Curve II), we deduce a molecular heat of vaporisation of approximately 14 kg.-cals.

Vapour pressure of bisdiethylantimony.

Temp.	89°	107°	118°	129°
p (mm. Hg)	0·7	1·6	2·9	4·2

Determination of the molecular weight in benzene showed no sign of dissociation. The obvious conclusion that the colour is not due to a partial splitting into free radicals seems all the more probable, for in such a case we should expect the ethyl compound to have a greater tendency to dissociate than the methyl compound and therefore to show a deeper colour, whereas the contrary is the case.

The ethyl compound is less readily oxidised by air than the methyl compound: it fumes but does not catch fire; the odour of the fume is also garlic-like.

Atmospheric oxidation of the benzene solution affords white *diethylantimonic acid*, $(C_2H_5)_2SbO\cdot OH$, which is odourless, soluble in water, insoluble in ether, and only slightly soluble in alcohol. Its reaction is neutral towards methyl-orange, acid towards phenolphthalein; it is reduced by stannous chloride, the characteristic odour of the tervalent antimony alkyls being produced.

The reactions of bisdiethylantimony with iodine and bromine are similar to those of the methyl compound, equivalent quantities of the halogens producing respectively (i) an orange solid and a yellow oil and (ii) a white solid and a pale yellow oil. The antimony content of the last corresponds to the formula $(C_2H_5)_2SbBr$.

In order to elucidate the reason for the colour of the bisdialkylantimony compounds, we attempted to apply our procedure to the synthesis of the *n*-propyl and the *iso*butyl compound, but although we took every precaution to shorten the track of the expected free radicals, *n*-propyl and *iso*butyl, we found no trace of their compounds with antimony. In agreement with a previous result (Part II, p. 2707), the main product was bisdimethylantimony.

III. *Reaction of Free Methyl and Free Ethyl with Bismuth.*—Since the action of free radicals on antimony had yielded substances which could not be prepared by the usual methods, it seemed probable that bismuth would yield corresponding compounds. As with arsenic and antimony, the behaviour of bismuth towards the free radicals depended on the temperature. Cold mirrors afforded only trialkyls, but with heated mirrors, there were formed, in addition, a difficultly volatile violet-red substance from free methyl and a black substance from free ethyl. The former melted below room temperature to a yellow oil and at once became transformed into a black solid; from its low volatility, as compared with trimethylbismuthine, and the similarity in colour to bisdimethylantimony, we conclude that this compound was bisdimethylbismuth. The black substance from free ethyl was apparently produced by spontaneous decomposition of initially-formed bisdiethylbismuth. These substances were not obtained in quantity sufficient for analysis, but they merit further investigation, for the bismuth analogues of cacodyl are not known (cf. Blicke, *loc. cit.*).

Summarising, it may be said that by the action of free methyl and ethyl on arsenic,

antimony, and bismuth, only such compounds were produced as were volatile under the conditions of experiment. In agreement with this is the fact that the molecular complexity of the products diminishes in passing from arsenic, through antimony, to bismuth. While the most volatile, arsenic, can form pentameric monoalkyls, such substances are formed with antimony only to a minor extent, and not at all with bismuth.

IV. *Reaction of Free Methyl and Free Ethyl with Beryllium.*—In disagreement with the foregoing regularity was the fact that free radicals had not hitherto been found to react with beryllium (Hahnfeld, Diss., Königsberg i. Pr., 1932, p. 15), although its alkyls do not possess a particularly low volatility : dimethylberyllium (Gilman and Schulze, *J.*, 1927, 2665) sublimes at 200°, and diethylberyllium boils at 110°/15 mm. Since beryllium could not be distilled in a high vacuum, its mirrors were produced by the thermal decomposition in a quartz tube of diethylberyllium,* freed from halogen by treatment with silver and silver oxide. In agreement with previous results, no reaction could be observed with either methyl or ethyl. This inertness did not arise from leakage in the apparatus, since lead mirrors placed before or after the beryllium mirror were readily removed, but must be attributed to impurity of the mirror—a conclusion strengthened by its dirty brown-black appearance. This could only originate from an attack of the beryllium on the quartz, although, according to Borchers (*Metallwirt.*, 1931, **10**, 863), such attack should only occur above 1400°. To eliminate the effect of the silica wall, a well-cleaned piece of gold foil, which had been ignited in hydrogen, was placed in the tube and tested for its inertness towards free radicals, and beryllium was deposited thereon in quantity sufficient to form a brilliant metallic layer. A current of hydrogen was then passed through the apparatus until no more diethylberyllium was given up by the tap grease. If free methyl, from the thermal decomposition of ethyl-lead at 950° (cf. below), or free ethyl was then led over the mirror at 150°, in both cases white substances condensed in the liquid-air-cooled U-tube following the quartz tube. The methyl product was solid at room temperature, but the ethyl compound melted below room temperature to a colourless liquid, according to the properties of dimethyl- and diethyl-beryllium respectively. Both substances in contact with the air formed white oxidation products in which beryllium was identified. Beryllium, therefore, is attacked by free radicals, and the generality of the above rule is established.

The compounds identified in this work are collected in the following table for convenience.

Compounds resulting from the action of free methyl and free ethyl on arsenic, antimony, and bismuth.

(The compounds surrounded by a frame are formed only when the mirrors are heated.)

Compounds.	Arsenic.		Antimony.		Bismuth.	
	Methyl.	Ethyl.	Methyl.	Ethyl.	Methyl.	Ethyl.
Trialkyls	$AsMe_3$	$AsEt_3$	$SbMe_3$	$SbEt_3$	$BiMe_3$	$BiEt_3$
Dialkyls	$[AsMe_2]_2$	$[AsEt_2]_2$	$[SbMe_2]_2$	$\boxed{[SbEt_2]_2}$	$\boxed{[BiMe_2]_2}$	
Monoalkyls	$[AsMe]_5$	$[AsEt]_5$				

EXPERIMENTAL.

The apparatus was essentially the same as that described in Part I. In order to increase the concentration of radicals, an alteration was made in that the vessel of tetramethyl-lead was maintained not at − 70° but at − 40°, and that of tetraethyl-lead at 0° instead of − 25°.

Care must be exercised that in the decomposition of tetraethyl-lead the temperature is not raised above 600°, otherwise the ethyl undergoes decomposition, forming methyl . at 800° this decomposition was quite appreciable, and at 950° it was total. This radical was identified by the action of the decomposition products on antimony and beryllium; bisdimethylantimony was formed (identified by m. p), and from beryllium a white solid was obtained which oxidised in the air, and in which beryllium was identified (for method, see below) : this could only have been dimethylberyllium, for the diethyl compound is liquid at room temperature.

For the identification of the substances obtained, the U-tube in which the products were

* For this compound we are indebted to the kindness of Prof. H. Gilman, State College, Ames, Iowa. (See also Gilman and Wright, *J. Amer. Chem. Soc.*, 1933, **55**, 2893.)

B B

condensed was connected to a fractionation apparatus consisting of three U-tubes, separated by taps. Each was furnished with a capillary for determination of the m. p. and b. p. by Emich's method (*Monatsh.*, 1917, **38**, 219), and also, by means of a ground joint, with a tube which served for the removal of the substance. Since, owing to their ready oxidisability, the substances here investigated had to be kept out of contact with the air, we distilled them into this tube, which was constricted in its lower portion to facilitate sealing off. From the difference in weight between the empty tube and the two parts of the tube after sealing off, the weight of the substance could be determined, due allowance being made for the air-free volume in the sealed-off portion.

The analyses for arsenic and antimony were made by titration with potassium bromate (Norton and Koch, *J. Amer. Chem. Soc.*, 1905, **27**, 1247).

IA. *Action of Free Methyl on Arsenic.*—(a) *With cold mirrors.* The chief products were colourless compounds which oxidised in the air and condensed in the liquid-air-cooled condensation tube. These were separated by fractional distillation, the three U-tubes of the apparatus being kept at − 26°, − 58°, and − 78°, and a very slow current of hydrogen being led through. At − 26° cacodyl condensed (m. p. − 6°, b. p. 165°) [Bunsen (*loc. cit.*) gives b. p. *ca.* 170°, m. p. − 6°; and Valeur and Gaillot (*Compt. rend.*, 1927, **185**, 779) give b. p. 163°, m. p. − 5°]. Trimethylarsine solidified at − 78° and had b. p. 74°/760 mm. [Cahours (*Annalen*, 1862, **122**, 338) gives b. p. *ca.* 70°; Renshaw and Holm (*J. Amer. Chem. Soc.*, 1920, **42**, 1468) 50·7—51·7°/ 747·5 mm.; Valeur and Gaillot (*loc. cit.*) 50—52°; Natta (*Chem. Zentr.*, 1927, I, 416) 68—73°; Dyke and Jones (*J.*, 1930, 2429) 51—53°]. Since this substance was always formed in our experiments in only very small amounts (2—3 mg.), it was not possible to effect a further fractionation.

At − 55° we obtained a substance, m. p. − 13°, which was apparently a mixture of both the foregoing compounds.

(b) *With heated mirrors.* The arsenic mirror was heated only at the end adjacent to the decomposition spiral, the temperature being such that the arsenic just did not distil away. The mirrors were then attacked a little beyond the spiral, where the temperature was no longer so high as to hinder reaction with the free radicals. When the arsenic was removed from this spot, the mirror was renewed. The cyclic pentamethylpentarsine separated in the quartz tube behind the mirror as a bright yellow oil, b. p. 193—200°/15 mm. Minute amounts of this oil were formed also from the cold mirror. The data in the literature for the b. p. of this substance are very discordant. Auger (*Compt. rend.*, 1904, **138**, 1706) found 190°/15 mm.; Steinkopf and Dudek (*Ber.*, 1928, **61**, 1908; see also Steinkopf, Schmidt, and Smie, *Ber.*, 1926, **59**, 1463), who termed the compound arsenomethane, found 190°/13 mm., and Palmer and Scott (*J. Amer. Chem. Soc.*, 1928, **50**, 536) found 178°/15 mm.; but Valeur and Gaillot (*loc. cit.*) give 190°/5 mm. The molecular complexity was determined by Steinkopf and his co-workers in various solvents as $(CH_3 \cdot As)_5$, and this was confirmed by Palmer and Scott (*loc. cit.*).

The oil smelt garlic-like, oxidised in the air, and when brought into contact with hydrochloric acid, changed into a red solid. It was deposited in the condensation tube also, along with the arsine, and here was transformed almost instantaneously into a dark red solid. It was difficult to obtain this substance entirely free from arsenic. After several experiments, 21·7 mg. of the compound had collected in the U-tube (Found : As, 82·3. Calc. for $CH_3 \cdot As$: As, 83·3%). In spite of the small quantity, therefore, it seems probable that in this case also pentamethylpentarsine was present.

In addition to these high-molecular substances, readily volatile colourless products resulted, which were separated by fractional condensation as described above, and identified as trimethylarsine and bisdimethylarsenic.

IB. *Action of Free Ethyl on Arsenic.*—(a) *With cold mirrors.* The least volatile substance formed was again a very small amount of yellow oil, which showed, however, no tendency to polymerise. The more volatile products were fractionated, the U-tubes being cooled to − 21°, − 36°, and − 55°. At − 36°, bisdiethylarsenic (b. p. 185—187°) condensed (Landolt, *Annalen*, 1854, **89**, 319, gives b. p. 185—190°). The material condensing at − 55° was again fractionated. It was kept at − 42° while the trap was cooled in liquid air, and the fractionation interrupted as soon as a portion had distilled over. The distillate was triethylarsine (b. p. 140·5°/736 mm.) (Landolt, *loc. cit.*, gives 140°/736 mm.; Dyke and Jones, *loc. cit.*, give 138—139°).

(b) *With heated mirrors.* A yellow oil, which showed but little tendency to polymerise in presence of hydrochloric acid, condensed behind the mirror and in the condensation tube. From its analogy with the methyl compound, it may be regarded as the cyclic pentaethylpentarsine. As it was obtained only in very small amount, no further identification was attempted,

especially since there is no record of its b. p. Besides this compound, triethylarsine and bis-diethylarsenic again resulted; these were separated and identified as described above.

IIA. *Action of Free Methyl on Antimony.*—In this reaction, irrespective of the temperature of the mirror, a mixture of trimethylstibine and bisdimethylantimony resulted. This was fractionated, the first two U-tubes being kept at — 15° and — 50°, while the last was cooled in liquid air. To accelerate the fractionation, a little hydrogen (*ca.* 0·35 mm.) was passed through the apparatus. Trimethylstibine, b. p. 82°, condensed in the last U-tube (Landolt, *J. pr. Chem.*, 1861, **84**, 329, gives b. p. 80·6°). In the tube at — 15°, *bisdimethylantimony* condensed as brilliant red needles, m. p. 17·5° [Found : Sb, 80·0, 79·8; C, 15·9; H, 4·2. Sb(CH₃)₂ requires Sb, 80·2; C, 15·8; H, 4·0%]; on oxidation in benzene solution, it gave dimethylantimonic acid (Found : Sb, 65·9, 65·9. Calc. : Sb, 65·9%).

By the addition of an equivalent amount of bromine, a bright yellow oil resulted which partly solidified; it was distilled off [Found : Sb, 53·1. Calc. for (CH₃)₂SbBr : Sb, 52·6%]. Addition of iodine gave a yellow oil (dimethyliodostibine), which also partly solidified.

We attempted to determine the molecular weight of bisdimethylantimony cryoscopically. As an indifferent atmosphere we used nitrogen, which was freed from oxygen by a simplification of Kautsky and Thiele's method (*Z. anorg. Chem.*, 1927, **152**, 342) {0·2405 g. of substance in 23·84 g. of benzene, gave Δt 0·161°; *M*, 319·6. 0·2977 g. in 24·05 g. of benzene, Δt 0·205°; *M*, 308. Calc. for [Sb(CH₃)₂]₂ : *M*, 303·6}. Since it might be expected that any dissociation would be more pronounced at higher temperatures, we carried out a molecular-weight deter-mination by Rast's micro-method (Found : *M*, 314·2, 313·1), and, although these determinations, on account of the smaller weights involved, were less accurate than those in benzene, they show that even at high temperatures dissociation does not occur.

IIB. *Action of Free Ethyl on Antimony.*—We confirmed Paneth and Lautsch's finding (Part II, p. 2707) that pure triethylstibine results from the action of free ethyl on a cold antimony mirror. At higher temperatures, however, several products occur in this case also, a mixture of a colourless oil and a yellow, less volatile compound being obtained. This was separated by fractional condensation, the U-tubes being cooled to — 13°, — 55°, and in liquid air. As in the separation of the methyl homologues, the fractionation was carried out in a slow stream of hydrogen (*ca.* 0·35 mm. Hg). White triethylstibine first distilled and condensed at — 55°, b. p. 159°/730 mm. (Löwig and Schweizer, *Annalen*, 1850, **75**, 327, give b. p. 158·5°/730 mm.). The fractionation was continued until the yellow substance condensing at — 13° showed a constant m. p. of — 61°. This was *bisdiethylantimony*. Since it was very difficultly volatile, it was not distilled over, but allowed to flow directly into a weighing tube and sealed off {Found : Sb, 68·0, 68·0; C, 26·5; H, 5·5; *M*, cryoscopic in benzene, 376·6, 376·6. [Sb(C₂H₅)₂]₂ requires Sb, 67·7; C, 26·7; H, 5·6%; *M*, 359·7}.

By the oxidation of bisdiethylantimony in benzene solution, *diethylantimonic acid*, (C₂H₅)₂SbO·OH, was formed as a colourless, odourless, amorphous substance (Found : Sb, 60·0. C₄H₁₁O₂Sb requires Sb, 59·6%).

Addition of equivalent amounts of iodine and bromine to bisdiethylantimony gave the corresponding diethylhalogenostibines. The iodo-compound was obtained, together with a yellowish-red solid, as a yellow oil, and the bromo-compound as a bright yellow oil from which a white solid separated (Found : Sb, 47·4. Calc. for C₄H₁₀BrSb : Sb, 46·9%).

III. *Action of Free Methyl and Free Ethyl on Bismuth.*—By using cold mirrors, we obtained trimethylbismuthine, b. p. 110—111° (Marquardt, *Ber.*, 1887, **20**, 1518, gives 110°; Schäfer and Hein, *Z. anorg. Chem.*, 1907, **100**, 298, give 106—107°), and triethylbismuthine, b. p. 112°/79 mm. (Marquardt, *loc. cit.*, gives 107°/79 mm.).

IV. *Action of Free Methyl and Free Ethyl on Beryllium.*—The detection of beryllium in the white products formed by atmospheric oxidation (see p. 369) was carried out by evaporating the substance to dryness with nitric acid and dissolving the residue in hydrochloric acid; on addition of quinalizarin and making the solution weakly alkaline, a cornflower-blue coloration at once resulted, and after some time a precipitate of the same colour was deposited. In the absence of beryllium the colour is violet-red.

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82. *Free Organic Radicals in the Gaseous State. Part V. The Reaction Products of Free Methyl in Hydrogen and Helium.*

By F. A. PANETH, W. HOFEDITZ, and A. WUNSCH.

THE mechanism of the reactions of free methyl and ethyl has already formed the subject of numerous investigations. Paneth and Hofeditz (*Ber.*, 1929, **62**, 1335) first described a method whereby the life period of free methyl could be determined, and made suggestions as to the order of the underlying reaction. In later communications, these investigations were repeated with greater accuracy, and extended to free ethyl (Paneth and Lautsch, *Ber.*, 1931, **64**, 2702, 2708; Paneth and Herzfeld, *Z. Elektrochem.*, 1931, **37**, 577; Hahnfeld, " Ueber das Reagieren freier organischer Radikale im Gaszustand," Diss., Königsberg i. Pr., 1932).

The significant result of the previous investigations was the recognition that the greater proportion of the free radicals disappears by a wall reaction. It was found that, by collision of free radicals with a mirror of a metal which yields a volatile alkyl compound, each encounter leads to adsorption of the alkyl, but that in a glass or quartz tube only 0·1% of the radicals striking the walls remains attached.

The experimental accuracy hitherto attainable has not sufficed to ascertain whether, and under what conditions, the free radicals disappear also by a homogeneous gas reaction. We have therefore introduced various improvements into the experimental arrangements rendering them more precise.

In addition to a more exact dosage of the free radicals and their source, tetramethyl-lead, we have paid special attention to the qualitative and quantitative examination of their reaction products. The free methyl radical was selected as the object of our investigation on the grounds that the reaction products to be expected in this case—methane, ethane, ethylene, hydrogen—are more readily determined qualitatively and quantitatively by the available methods of gas analysis than the less volatile end-products of the transformation of ethylene.

We now find that in hydrogen the free methyl disappears partly according to the equation : $CH_3 + H_2 \longrightarrow CH_4 + H$ (probably in a homogeneous reaction) and partly in the wall reaction : $CH_3 + CH_3 \longrightarrow C_2H_6$. The relative proportion of the two reactions depends on the concentration of the radicals and on the temperature; low concentration and heating diminishes the formation of ethane and favours that of methane. In helium, instead of hydrogen, the first reaction is excluded, and ethane is the main product; by using helium as carrier gas and maintaining a temperature of 500° the half value period of free methyl can be raised to 0·1 second.

EXPERIMENTAL.

I. *Improved Experimental Arrangements.*—The apparatus used and the method of measuring the half-life period were the same in principle as were described in Part I (*loc. cit.*). As well as other improvements in the apparatus, however, particular stress was laid upon maintaining the experimental conditions constant and strictly reproducible. The improvements made in accordance with this requirement took the form, first, of the provision of uniform streaming conditions and of uniform conditions of observation of the measurement mirror (variations in lighting could readily introduce errors of over 10% here). Above all, however, attention was paid to the uniform dosage of the tetramethyl-lead vapour, a factor which was a continual source of variation in the experimental results, and of which the control presented the most obstinate difficulties. On account of the importance of this point for the trustworthiness of the entire experimental method, we describe the form of tetramethyl-lead vaporising vessel found most suitable (Fig. 1).

The carrier gas enters through a narrow capillary K_1, 10—15 cm. long, placed immediately following the inlet tap 1. The gas streams first through the pre-cooling spiral, which is placed together with the tetramethyl-lead vessel in a cooling bath, and then passes through a layer of copper wool in which the tetramethyl-lead is distributed. Here it is charged with the vapour of the lead alkyl, in amount depending on the temperature of the bath, and finally leaves the vaporising vessel through the capillary K_2 and the tap 2.

The capillary K_2 is chosen to let through just that quantity of gas corresponding to the conditions of the experiment, while K_1 is arranged to pass a trifle more gas. There is thus always maintained in the vaporising vessel the pressure of the main transport gas supply, which is kept constant. The slow passage of the as yet unexpanded gas through the copper wool, which is kept at constant temperature within $0.1°$, together with the pre-cooling of the gas to the temperature of the bath, effects a uniform impregnation with the lead alkyl. The capillaries placed in both the inlet and the outlet tube immediately adjacent to the vaporising vessel prevent the contamination of the grease of the taps with lead alkyl vapour, which had previously been a persistent source of error. Accordingly, the filling of the vaporising vessel with tetramethyl-lead was carried out by distillation in a high vacuum through the side tube S, which was afterwards sealed off. Over-night, and during periods of disuse, the inner part of the vaporising vessel was kept at liquid-air temperature (Dewar vessel shown dotted). Variation of the gas stream in the apparatus was achieved by insertion of additional capillaries (K_3, K_4) connecting the measurement tube directly to the carrier gas lead.

Lead mirrors produced under similar conditions and during the same time with the foregoing experimental arrangements show by their appearance alone the serviceability of the method. Objective confirmation must be provided, however, by quantitative determination of the deposited lead. Hahnfeld (*loc. cit.*), in experiments on ethyl, in hard-glass tubes, weighed the mirror directly by cutting it out and determining the loss in weight on dissolution of the lead. Owing to the higher temperature necessary for the decomposition of tetramethyl-lead, however, the use of quartz tubes was necessary, so this method could not be applied.

Of the methods available for the determination of small quantities of lead, the colorimetric determination as sulphide appeared most suitable for our purpose (for details, see Wunsch, Diss., Königsberg, 1933); mean values of several determinations on each solution were used and were accurate within 3%.

II. *Influence of Temperature on the Rate of Disappearance of Free Methyl.*—With this apparatus we first accurately determined a half-life curve of free methyl at room temperature, in hydrogen at 1—2 mm. pressure with a stream-

FIG. 1.

ing velocity of 1035 cm. per sec., using a quartz tube 170 cm. long and 1 cm. in diameter. At the end of the tube, a lead mirror was allowed to deposit for 3 minutes in the usual way (temperature of vaporising vessel, $-52°$). This was then removed, by the action of free radicals from varying distances, the mirror being observed always under the same conditions of illumination. The reciprocal of the duration of the removal process, $1/d$, was used as a relative measure of the activity, A, of the radicals.

The streaming velocity was calculated from the volume of hydrogen passing through the apparatus in unit time. The time elapsing between the moment of formation of the free radical and its reaction with the mirror may be calculated from the streaming velocity, allowance being made for the fall of pressure in the measurement tube (cf. Part III, *loc. cit.*, note 4, p. 2709). The results of the measurements are given in Table I (a), where s is the time interval between formation and reaction, and D the distance between the place of formation and that of reaction.

As may be seen by comparison with the earlier measurements of the life period, we have extended the range of our measurements about four-fold (to 106.8×10^{-3} sec. as against 26×10^{-3} sec.). The fact now emerges that if—as in the former work—log A be plotted against s (Fig. 2, curve I), the plot is no longer a straight line, *i.e.*, the disappearance of free radicals from the
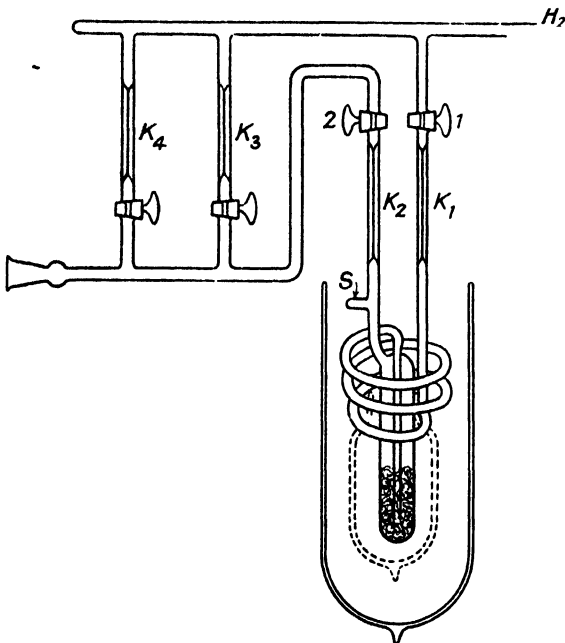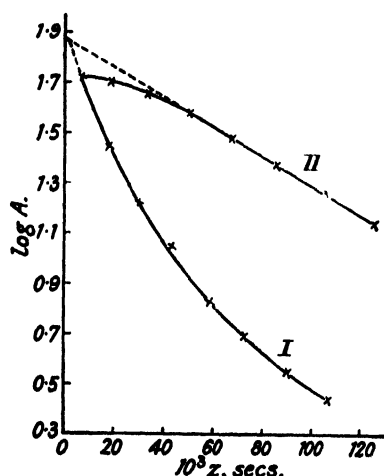
TABLE I.

D, cm.	z × 10³, secs.	d, secs.	A = 10⁴/d.	log A.	D, cm.	z × 10³, secs.	d, secs.	A = 10⁴/d.	log A.
	(a) *Tube at 20°.*					(b) *Tube at 350°.*			
10	6·8	190	52·63	1·721	10	6·6	190	52·62	1·7212
25	17·5	360	27·78	1·444	25	18·1	200	50·00	1·6990
42	30·0	600	16·67	1·222	42	33·1	220	45·45	1·6576
59	43·1	900	11·11	1·046	59	50·0	260	38·46	1·5850
78	58·4	1500	6·67	0·824	78	67·0	330	30·31	1·4815
95	72·7	2040	4·90	0·690	95	85·4	420	23·81	1·3768
115	90·1	2820	3·55	0·550	115	105·6	540	18·52	1·2676
133	106·8	3600	2·78	0·444	133	125·6	720	13·89	1·1427

gas does not follow the unimolecular law. Owing to the shorter range of measurement and the strong scattering of the individual points in the former work, this was not apparent.

We then determined whether the wall reaction, which is principally responsible for the disappearance of free radicals, could be suppressed. Experience indicates that with increase in the wall temperature of the tube, the accommodation coefficient would decrease, thereby lengthening the life of the free radical. Measurements were carried out exactly as described above, the tube between the point of formation of the radicals (Fig. 3A, a and b) and the measurement mirror (e) being heated electrically (c). It was necessary to leave unheated a length of 5 cm., d, immediately preceding the mirror.

FIG. 2.

It was established that the life of the radicals did, indeed, increase with rising temperature. Working in a stream of hydrogen, the optimum life period under the experimental conditions used by us was attained with a wall temperature of 350—360°. If the temperature were raised further, the life of the radicals again decreased. It appears that a new reaction assumes prominence, which with rising temperature leads to an ever-increasing destruction of the radicals.

The values obtained under the optimum conditions are collected in Table I (b). In calculating z, allowance has been made for the fact that, owing to the thermal expansion of the carrier gas, the pressure and velocity conditions are somewhat different from those obtaining in cold-tube experiments. Accordingly, the values of z differ somewhat from those in Table I (a) despite identical values of D.

FIG. 3A.
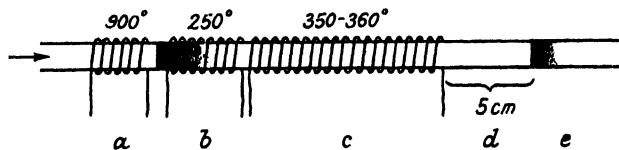
FIG. 3B.
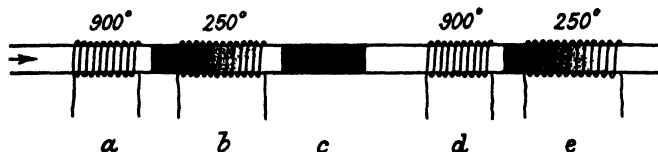
The values obtained, plotted in the same way as before (Fig. 2, curve II), form a straight line; only the first three points show an increasing deviation in the direction of the time interval zero. This deviation is to be attributed to the experimental arrangement, since (as stated above) the tube could not be heated right up to the measurement mirror. At this section of the tube, however, as follows from the cold-tube experiments, the radicals are especially rapidly

destroyed. Although the influence of this unheated 5 cm. is inappreciable with great distances between the decomposition point and the measurement mirror, yet, as this distance diminishes, the strong radical-destroying effect of this section of tube becomes increasingly perceptible. The activities fall more and more below the calculated values, and the curve assumes an increasingly downward curvature. The first point is common to both curves, as is to be expected, since this was obtained under the same conditions for both. It is to be anticipated, further, that both curves if extrapolated back to the zero point (as in the broken lines) would again meet in the same value for A, since the point $z = 0$ corresponds to the point of decomposition of the tetramethyl-lead. At this point, the extrapolated activities, under otherwise identical conditions of dosage, should be the same. The curve accords with this requirement. From the slope of curve II, the half-value period T of free methyl under the conditions specified is $5 \cdot 2 \times 10^{-3}$ sec.

Consideration of the curves I and II suggests that the deactivation of the free radicals proceeds by two distinct reactions. The first, preponderant at room temperature, decreases with rising temperature and *vice versa*, since experiment shows that no free radicals pass if a point on the tube is chilled with liquid air. The vapour pressure of the methyl radical (which presumably does not differ much from that of methane) is far too high at liquid-air temperature for this to be due entirely to a freezing out of the radicals. The other, as yet hypothetical, reaction by which the free radicals disappear, increases with rise in temperature. Up to 350°, the decrease in the first reaction outweighs the increase in the second, so that the life of the methyl radical shows a net increase. Above 350°, the disappearance of radicals by the second reaction becomes so great that the life decreases again.

III. *The Reaction Products of Free Methyl in Hydrogen.*—An investigation of the reaction products under various conditions was undertaken to ascertain the nature of the reactions, and to what extent they are responsible for the disappearance of the free radicals.

For this purpose we developed a technique which enabled the reaction products to be collected quantitatively during continuous running, without altering any of the foregoing conditions of experiment (cf. the collection of products during intermittent running, Simons, McNamee, and Hurd, *J. Physical Chem.*, 1932, **36**, 939). On the supposition that the recombination products would be principally gases of low b. p., no success could be anticipated from a simple condensation in liquid-air-cooled traps. Filling the condensation tubes with adsorbent charcoal was not practicable, since the streaming velocity must be maintained at its former rate. We accordingly constructed tubular copper-gauze cylinders, packed with active charcoal, which were so arranged in wash-bottle-like traps that the gas stream could flow over both their inner and outer surfaces (Fig. 4). We established that a measured volume of methane, added to the hydrogen, was removed quantitatively from the gas by the traps, which were cooled externally by liquid air. After replacing the cooling bath by boiling water, the gas could be quantitatively extracted by means of a Töpler pump, and estimated. As a result of this test, we could safely assume the complete absorption of the expected gaseous products.

With this experimental arrangement, we first carried out four runs during which the vaporising vessel was kept at − 31°, and the tetramethyl-lead quantitatively decomposed (cf. Part I, *loc. cit.*, p. 1340). The pressure at the decomposition point·was 1·6 mm. throughout. The analyses of the gas mixtures so obtained are set out in Table II. By comparison of the quan-

Fig. 4.
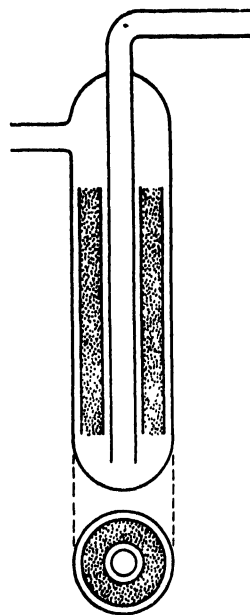
TABLE II.

Duration of expt., hrs.	Pb deposited, mg.	Gas obtained, c.c.	C_2H_4, %.	C_2H_6, %.	CH_4, %.	CH_3, c.c., calc. from amount of Pb	CH_3 found, c.c.
8¼	278·7	78·6	0·5	40·9	58·6	121·0	111·0
8	—	—	0·9	42·8	56·3	—	—
7½	256·6	68·1	0·9	42·5	56·7	111·0	97·6
8	265·3	70·0	0·6	42·3	57·1	114·8	100·0

tities of gas found (converted into its equivalent amount of free methyl) with those calculated from the simultaneously determined weights of deposited lead, it may be seen that about 10% of the expected gases escape measurement. The origin of this loss we take to be, on the one hand, a complete disruption of the methyl, recognisable by the deposition of carbon in the decomposition zone, and on the other hand, the invariable formation of perceptible amounts of oily products which cannot afterwards be recovered from the adsorbent charcoal. The average composition of the gases we found to be : C_2H_4, 0·7; C_2H_6, 42·1; CH_4, 57·2%. Taking into account that for the formation of each molecule of ethylene or ethane, two methyl radicals have disappeared, while for methane only one is required, the above figures can be so converted as to show what percentage of the radicals present is used up in forming each of the three gases named. The proportions are C_2H_4, 1; C_2H_6, 59; CH_4, 40%, so a high proportion of methyl is used up at room temperature in the formation of methane.

Having obtained the above concordant results, we investigated the manner in which the relative proportion of the reaction products was dependent upon the concentration of the radicals. The temperature of the vaporising vessel was varied from − 1° to − 50°, other conditions being maintained constant. The pressure was 1·4—1·6 mm., and the streaming velocity 1140 cm. per sec., 821 × 10^{-7} g.-mol. of hydrogen flowing through the apparatus per sec. The results are collected in Table III (a). It will be seen that, on using low concentrations of tetramethyl-

TABLE III.

Temp. of bath.	Duration of expt., hrs.	Pb deposited, mg.	Gas obtained, c.c.	PbMe₄ decomp. per sec. mols. × 10⁹.	$\dfrac{10^5 PbMe_4}{H_2}$.	Gas analysis, %.			Per cent. of CH₃ disappearing as		
						C_2H_4.	C_2H_6.	CH_4.	C_2H_4.	C_2H_6.	CH_4.
(a) *Tube at 20°.*											
− 1°	1	271·6	71·0	364·0	444·0	2·4	49·5	48·0	3·1	65·3	31·6
−15	3	382·8	100·5	171·0	208·0	1·7	50·0	49·3	2·3	65·8	31·9
−25	6½	296·4	80·4	61·3	74·6	1·0	48·1	50·9	1·4	64·4	34·2
−31 *	8	266·9	72·2	45·0	54·8	0·7	41·9	57·5	1·0	59·0	40·0
−45	12½	102·5	24·7	11·0	13·4	0·0	37·5	62·5	0·0	54·5	45·5
−48	20	133·4	35·2	8·9	10·9	0·0	32·1	67·9	0·0	48·6	51·4
−50	24	125·2	—	7·0	8·5	0·0	28·9	71·7	0·0	44·8	55·2
(b) *Tube at 350°.*											
− 1	1	190·0	54·3	392·0	466·0	2·2	43·8	54·0	3·0	60·0	37·0
−19	1½	153·3	44·4	.138·0	168·0	1·5	35·2	63·3	2·2	51·5	46·3
−31	5¼	—	—	—	—	0·8	26·9	72·3	1·2	42·1	56·7
−31	5	178·0	58·1	47·5	58·0	0·8	27·4	71·8	1·2	42·7	56·1
−48	20	126·0	37·0	8·5	10·3	0·2	10·2	89·6	0·3	18·9	81·2

* The value for −31° is the mean of the values in Table II.

lead (PbMe₄ : H₂ = 8·5 × 10^{-5}), 45% of the radicals disappear as ethane and 55% as methane. With higher concentrations (444 × 10^{-5}), these values are 65% and 32% respectively. The amounts of ethylene (3%) also formed at the higher concentrations are of secondary importance. In view of the considerable amount of energy required to form ethylene and hydrogen from two methyl radicals (cf. Simons, McNamee, Hurd, *loc. cit.*, p. 945), their origin may be attributed to the hot (*ca.* 900°) decomposition zone.

We investigated also the products resulting from the disappearance of free radicals under the same conditions, but in a tube heated to 350—360°. For this purpose, the quartz tube was furnished for its entire length with a furnace winding, so that the radicals must decay over a length of 130 cm. according to the reaction scheme valid under hot-wall conditions. This displacement of the results as compared with decomposition in the cold tube may be seen from Table III (b).

In this instance, with low tetramethyl-lead concentrations (10·3 × 10^{-5}), 18·9% disappears in the form of ethane and 81·2% as methane, while with higher concentrations (466 × 10^{-5}) the proportions are 60% and 37% respectively : heating of the tube evidently favours the formation of methane both at low and at high concentrations. Moreover, only a small proportion of the radicals had the opportunity to decompose according to the hot-wall scheme, while the greater part underwent decomposition in the further part of the apparatus by the reactions obtaining in the cold tube. To secure complete decomposition in a hot tube it would have been necessary either to employ a disproportionately long tube, since the life in a hot tube

is longer (Fig. 2), or else to lower the streaming velocity. The latter was not possible if other conditions were to remain constant.

To form some conception of the reactions occurring under the conditions employed in the life-period determinations given in Table I and Fig. 2, the values for the percentage of methyl forming methane (from Table III) were plotted against the concentrations of tetramethyl-lead employed, and extrapolated to a lead alkyl concentration of 2×10^{-5}. (With the minute lead alkyl concentrations employed in these determinations, the collection of the quantity of gas required for analysis would have occupied too long.) Fig. 5 shows the curves obtained—I and II being derived from Table III a and b respectively.

FIG. 5.

$10^8 \times PbMe_4/H_2.$
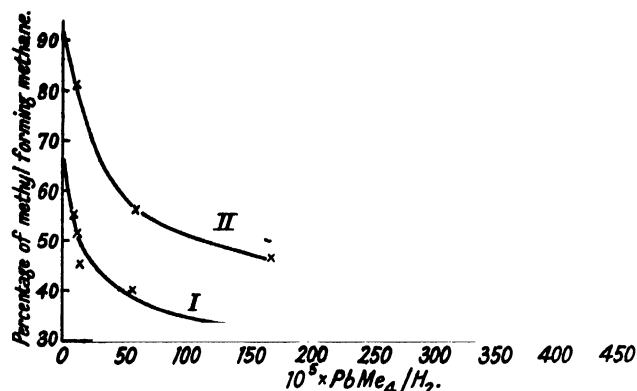
The extrapolated values indicate that, under the conditions obtaining during the determination of the half-value curve in the cold tube, 60% of the radicals disappeared as methane and 40% as ethane. In the hot tube, however, 90% formed methane and 10% ethane.

IV. *Influence of Concentration on the Yield of Free Methyl.*—The effect of temperature on the course of the reaction having been ascertained, it was important to investigate whether an appreciable fraction of the radicals was already destroyed in the hot decomposition zone.

In order to ascertain the maximum yield of free radicals resulting from the decomposition of tetramethyl-lead, a mirror of lead at least 3 cm. long was produced on the wall of the tube by distillation of the metal (Fig. 3B). Directly in front of this mirror (c) tetramethyl-lead was decomposed by a spiral (a) combined with a " quantitative decomposition spiral " (b). The resulting radicals reacted with the lead mirror (c) and the newly formed lead alkyl was again quantitatively decomposed by spirals d and e.

If the tetramethyl-lead were to split off 100% of its methyl content in the form of free radicals, one would anticipate that the lead deposited at the point of origin of the radicals would be equal in amount to that, derived from the mirror (c), which separates upon the second pair of spirals. Comparison of the amount of primary lead, originating from the decomposition of the lead alkyl, with the secondary deposit on the second pair of spirals, which has been transported by the free radicals, enables the yield of free radicals actually obtained to be estimated. The lead was determined colorimetrically as before.

TABLE IV.

$10^8 PbMe_4/H_2.$	Lead I, mg.	Lead II, mg.	Yield of radicals, %.	$10^8 PbMe_4/H_2.$	Lead I, mg.	Lead II, mg.	Yield of radicals, %.
21·4	7·330	3·500	48	2·0	0·686	0·530	77
9·1	3·110	1·806	58	1·5	0·510	0·396	78
5·7	1·949	1·349	69	1·5	0·508	0·419	82
2·6	0·882	0·648	74				

The results are collected in Table IV. Lead I represents the amount of lead deposited in the formation of the radicals, and Lead II that transported by the radicals.

The yield of free radicals is seen to rise to 82% as the concentration of tetramethyl-lead used is decreased. Similar experiments have already been carried out with free ethyl with essentially the same result, *i.e.*, 83% (Hahnfeld, *loc cit.*). It is very likely that in both cases

the use of helium instead of hydrogen as carrier gas will permit of an even nearer approach to 100%.

The decrease in the yield of radicals with increasing concentration may be explained primarily as a result of the greater frequency of collisions within the hot decomposition zone, whereby the radicals are more rapidly transformed into stable products which do not react with lead. The formation of ethylene at higher concentrations, previously detected, confirms this view. Moreover, the tarry products then resulting in greater amount protect the lead from attack by the radicals, and indicate falsely a lower yield of free radicals.

An important conclusion drawn from the results collected in Table IV, taken in conjunction with the observations already referred to, is that even at room temperature free methyl is capable of reacting with the carrier gas, hydrogen. We have now established that at a tetramethyl-lead concentration of 2×10^{-5}, about 80% of the radicals are still effective behind the decomposition point. Under the same experimental conditions, it appears from curve I (Fig. 5) that at room temperature, 60% of the resulting radicals produce methane and 40% ethane. Even if it be assumed that the 20% of the radicals destroyed within the decomposition zone had given rise to the quantitative formation of methane, there still remains 40% of methane which must necessarily have been formed from methyl and hydrogen in the remainder of the apparatus almost at room temperature, although the gas may be slightly hotter than the walls of the tube.

Our experiments scarcely admit of any interpretation other than that the greater proportion of the methyl radicals disappear at room temperature in the reaction $CH_3 + H_2 \longrightarrow CH_4 + H$. We will not here discuss certain theoretical objections arising from other work. We may point out, however, that the straight line in curve II (Fig. 2) can easily be explained, since in the hot tube the above unimolecular reaction predominates. On the other hand, in the cold tube the order of the wall reaction must depend on the concentration of the already adsorbed radicals, and may therefore deviate from the unimolecular (curve I).

V. *The Reaction Products of Free Methyl in the Absence of a Carrier Gas.*—From the facts thus far ascertained, it follows that, in the absence of hydrogen as carrier, ethane should predominate as the product of reaction. To investigate this, the vapour of tetramethyl-lead was admitted directly to the apparatus. The pressure and velocity of the gases passing through the quartz tube were in this case less than in the previous experiments. Thermal decomposition was effected in one series quantitatively (Expt. A, Table V), and in another series (B, Table V) without using a quantitative decomposition spiral, in order to ascertain whether any reaction could be detected between free methyl and the regenerated lead alkyl produced by its attack on its own lead mirror.

TABLE V.

Group.	Duration of expt., hrs.	Press., mm. Hg.	Pb deposited, mg.	Gas obtained, c.c.	PbMe$_4$ decomp. per sec., mols. $\times 10^9$.	Gas analysis, %.			Per cent. of radicals disappearing as		
						C$_2$H$_4$.	C$_2$H$_6$.	CH$_4$.	C$_2$H$_4$.	C$_2$H$_6$.	CH$_4$.
A	10	0·017	214·6	50·0	28·8	2·7	89·1	8·2	2·8	93·0	4·2
B	10	0·017	—	—	28·8	2·1	91·0	6·9	2·2	94·2	3·6
A	¼	0·112	280·6	60·3	754·0	5·4	78·8	15·8	5·9	85·5	8·6
B	¼	0·112	—	—	754·0	4·1	80·4	15·5	4·5	87·2	8·3

Analysis showed ethane to be the chief product. Ethylene was present in rather larger amount than in experiments with hydrogen as carrier, which may have been due to the lower streaming velocity. The radicals remain longer in the heated zone, and so have more opportunity to form ethylene, as already mentioned. The origin of the methane also is to be sought in the hot decomposition zone. It is conceivable that the free methyls, by dehydrogenation, reduce other methyl radicals to methane.[*] A complete dehydrogenation of the radicals, for instance, is shown by the considerable deposition of carbon. For the same reason, the percentage of methane formed rises with the amount of tetramethyl-lead decomposed in unit time, since—owing to the higher pressure—the free path of the radicals is smaller, and the time spent in the hot part of the tube greater.[†]

VI. *The Reaction Products of Free Methyl in Helium.*—It was to be anticipated from the

[*] Such a process is called in German chemical literature " Disproportionierung."

[†] These observations agree with those of Simons, McNamee, and Hurd (*loc. cit.*), who also decomposed tetramethyl-lead by a streaming method in the absence of a carrier gas, and obtained an even larger methane content, inasmuch as they worked at still higher pressures (1·5—2 mm. Hg).

foregoing results that by choice of an inert carrier gas, ethane would again be found to be the chief reaction product of the free methyl radicals. To this end, we replaced the hydrogen as carrier gas by helium, the streaming velocity being 650 cm. per sec., and the pressure in the measuring tube about 1·3 mm. The results obtained are given in Table VI. The displace-

TABLE VI.

Temp. of bath.	H_2.	Gas analysis, %. C_2H_4.	C_2H_6.	CH_4.	Per cent. of radicals disappearing as C_2H_4.	C_2H_6.	CH_4.
− 1°	0·9	2·8	87·0	9·3	2·9	92·1	5·0
−25	1·0	1·7	89·5	7·8	1·9	94·1	4·0

ment of the reaction towards the side of ethane formation is seen. Although the pressure in the decomposition tube was greater than in the experiments without a carrier gas, the yield of methane was smaller, since the helium acted as a diluent in diminishing the interaction of the radicals in the hot section of the tube.

VII. *The Life Period of Free Methyl.*—We have seen that, at room temperature in an atmosphere of hydrogen at 1—2 mm. pressure, free methyl disappears by one reaction leading to ethane, and by another giving methane; also that the proportion of the reaction giving rise to ethane may be diminished by heating the wall of the tube. Further, by the choice of an inert gas as the carrier gas, the reaction yielding methane can be practically inhibited. It follows that by the simultaneous use of an elevated temperature and of an inert carrier gas, a means should be provided of extending the life of free methyl.

As our experiments showed, the concentration of free radicals in a stream of helium does, indeed, decay much more slowly in a hot tube than in a cold; *e.g.*, at a distance of 105 cm. from the point of formation, and with a streaming velocity of 650 cm. per sec., it took 71 mins. for the disappearance of a 3-minute measurement mirror when the tube was cold, as against only 7 mins. with the tube hot. It is remarkable that the life of the free methyl did not attain its maximum at 360° in this case, as happens when hydrogen is the carrier gas, but that the highest temperature used by us, a red heat (*ca.* 500°), was found to be best. The temperature could not be raised higher because of experimental difficulties. It is to be expected, however, that the optimum temperature for the life of free methyl would be attained immediately before the inception of a cracking process.

To determine the half-value period, we carried out a number of activity measurements at different distances in the heated tube. The results given in Table VII were thus obtained.

TABLE VII.

D, cm.	$z \times 10^3$, sec.	d, secs.	$A = 10^4/d$.	$\log A$.	K.	D, cm.	$z \times 10^3$, sec.	d, secs.	$A = 10^4/d$.	$\log A$.	K.
21	32·8	170	58·8	1·769	7·4	62	97	265	37·7	1·576	7·0
35	54·5	190	52·7	1·722	6·8	104	162	420	23·8	1·376	

From the mean value of the reaction constant ($K = 7·0$), the half value period for the methyl radical under the conditions specified may be calculated to be 0·1 sec. If the accommodation coefficient α be calculated therefrom by the formula of Paneth and Herzfeld (*loc. cit.*), it is found to be but one-tenth of that obtaining in the cold tube : of 10,000 molecules striking the walls, only one is not reflected.

It was possible, therefore, in a tube 1 cm. in diameter, heated to 500°, and with an inert gas as carrier, to prolong the life of the methyl radical to about the same order of magnitude as that of atomic hydrogen. We have no doubt that under still more favourable conditions, the existence of free methyl might be prolonged still further above the half value period of 0·1 sec. now found.

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83. *Free Organic Radicals in the Gaseous State. Part VI. Attempts to prepare Various Free Radicals : the Existence of Free Benzyl.*

By F. A. PANETH and W. LAUTSCH.

OUR attempts to prepare free radicals other than methyl and ethyl (described in previous communications) having had to be temporarily abandoned, we report some results because in one instance a new free radical (benzyl) of comparatively long life has been found, and in other cases there are definite indications that the desired radicals are much less stable than free methyl or ethyl, if capable of existence at all.

I. *Attempts to prepare Free Propyl.*—As already mentioned (Part II, *Ber.*, 1931, **64**, 2707), we decomposed tetra-*n*-propyl-lead at about 400°, using exactly the same method as that yielding free methyl and ethyl, and investigated the action of the products upon mirrors of lead, antimony, and zinc.

With lead, a yellow liquid was produced (presumably chiefly a trialkyl-lead, since the tetra-alkyls are volatile) which decomposed above 100° with separation of metallic lead and formation of minute amounts of a liquid non-volatile in vacuum at room temperature. Antimony yielded a compound which, as judged by the colour, was bisdimethylantimony (Part IV). With zinc, in addition to hydrocarbons, there was formed chiefly dimethylzinc, identified by its m. p. and inflammability in air. It is possible that a higher zinc alkyl was also produced in traces.

From these experiments it follows that free propyl, which must be assumed to be formed transiently in the decomposition of tetrapropyl-lead, very rapidly decomposes, at least for the most part, producing considerable quantities of free methyl. It seems probable that the decomposition follows the equation $CH_3 \cdot CH_2 \cdot CH_2- \longrightarrow CH_3- + C_2H_4$ (cf. Rice, *Trans. Faraday Soc.*, 1934, **30**, 152).

Since we had observed (see Part IV, p. 369) that elevation of the temperature above 600° sufficed to decompose free ethyl completely into free methyl, it seemed likely that the decomposition of the free propyl might be due to the high temperature of the decomposition zone. We therefore attempted to lower the decomposition temperature of the tetra-*n*-propyl-lead by the use of catalysts (lead and copper). These attempts were fruitless, as also were attempts to produce free propyl by the electrical decomposition of tetra-*n*-propyl-lead vapour by means of high-frequency discharges.*

II. *Attempts to prepare Free Butyl.*—By the decomposition of tetra*iso*butyl-lead at about 300°, there resulted a reactive agent which attacked antimony mirrors. As with propyl, however, the resulting product consisted chiefly of bisdimethylantimony. It follows that, like free *n*-propyl, the *iso*butyl freed momentarily decomposes with formation of free methyl.

III. *Attempts to prepare Free Phenyl.*—Tetraphenyl-lead was decomposed in a hydrogen stream, at 2 mm. pressure, at a red heat. The lead mirror formed showed no sharp edge on the side remote from the flame, thus precluding the formation of an " aggressive " agent (cf. Part I, p. 1339). Lead and tellurium mirrors deposited a short distance away were not attacked, either when cold or when hot. Since carbon was deposited at the place of decomposition of the tetraphenyl-lead, the phenyl apparently underwent extensive decomposition without giving rise to free radicals of appreciable life.

We attempted also to obtain free phenyl by the action of sodium vapour on bromobenzene, using for the purpose a simplification of the technique developed by Horn, Polanyi, and Style (*Naturwiss.*, 1932, **20**, 401; *Z. physikal. Chem.*, 1933, B, **23**, 291). A tellurium mirror a short distance from the reaction zone served as a test for resulting free phenyl. Since this was not attacked either in the cold, or when hot, we must conclude that free phenyl either has a much shorter life than methyl or ethyl, or else does not attack tellurium.

The existence of free phenyl seems to be indicated by recent experiments of Horn and Polanyi (*ibid.*, 1934, B, **25**, 151; cf. also *Trans. Faraday Soc.*, 1934, **30**, 199). These authors also allowed bromobenzene to react with sodium vapour, the reaction products being caused

* We had previously observed (cf. Part I) that electrical discharges in a mixture of methane and hydrogen produced free radicals. These experiments were continued by Hofeditz, but are not yet published. The essential result is that glow discharges (50 cycles) in pure methane, as well as in mixtures of methane with various hydrocarbons, alcohols, and ethers, produce free radicals. These may be readily detected beyond the discharge by their action on metallic mirrors, if a stream of gas at about 1 mm. pressure is passed through the discharge tube at a velocity of 10—20 m. per sec.

to impinge upon iodine. They assumed the presence of iodobenzene in the organic reaction products, since they could not detect aliphatic iodo-compounds in the organically bound iodine. It is surprising that, with this experimental arrangement, the life of the phenyl appears to be not notably shorter than that of methyl or ethyl in similar experiments. In view of the interest attaching to the preparation of free phenyl, a more direct analytical identification of the iodobenzene is clearly desirable.

IV. *Attempts to prepare Free Methylene.*—We first attempted to obtain methylene by the decomposition of keten. This seemed hopeful, since Schmidlin and Bergmann (*Ber.*, 1910, **43**, 2821) have shown that above 600° acetone yields, not keten (reaction *a*), but ethylene, the formation of which can be most simply explained by the disruption of keten and transient formation of the free methylene radical (reaction *b*) :

$$(a)\ CH_3 \cdot CO \cdot CH_3 \longrightarrow CH_2 : CO + CH_4;\quad (b)\ 2CH_2 : CO \longrightarrow C_2H_4 + 2CO.$$

By passing keten in a rapid gas stream through a strongly heated quartz tube, we were unable to raise the temperature sufficiently to effect any appreciable decomposition, with formation of free methylene. As the following shows, however, free methylene decomposes at relatively low temperatures, with separation of carbon (compare also Williamson, *J. Amer. Chem. Soc.*, 1934, **56**, 2216). In the experiments with keten, this was never observed.

Another reaction in which the intermediate formation of free radicals is probable is the decomposition of diazomethane, which often reacts as would be expected of free methylene, *e.g.*, $CH_2N_2 + I_2 = CH_2I_2 + N_2$, $CH_2N_2 + R \cdot CO_2H = R \cdot CO_2CH_3 + N_2$. Staudinger and Kupfer (*Ber.*, 1912, **45**, 501, 504, 508) have already attempted to capture by means of carbon monoxide the nascent methylene formed by passing diazomethane through a heated silica tube, and indeed obtained keten in very small amounts, apparently according to the equation $CH_2 + CO = CH_2 : CO$. The transient formation of methylene is thereby virtually proved, but no information is gained as to its stability.

We passed diazomethane through a quartz tube, heated to 600° over a length of 15 cm., using first hydrogen and then helium as transport gas. Any methylene so formed we sought to identify by passing the products of pyrolysis over benzoic acid, but could detect no smell of methyl benzoate. Carbon mirrors were also unattacked, although one might expect the formation of allene, $CH_2 : C : CH_2$, by free methylene; as the diazomethane was quantitatively decomposed, presumably with initial formation of free methylene, we must conclude that the methylene radical is very unstable.

Since the hot quartz wall was possibly responsible for the disappearance of the methylene primarily formed, we also decomposed diazomethane by electric discharges, to exclude the influence of temperature. A solid product, rich in carbon, was formed, but methylene could not be detected.

A further possibility for the production of methylene lay in the gas reaction $CH_2Cl_2 + 2Na = CH_2 + 2NaCl$, studied by von Hartel and Polanyi (*Z. physikal. Chem.*, 1930, *B*, **11**, 97). An advantage of this reaction is its applicability at relatively low temperatures. We carried out the experiment in a helium atmosphere, taking care to cool the tube rapidly behind the place where the sodium vapour and methylene chloride diffused into one another, in order to preserve any methylene formed. Here also, considerable deposition of carbon occurred even at 300°, from which one must conclude that the methylene formed initially decomposes further on collision with the wall, if not before. Various alterations in the reaction conditions (altered concentration of the reacting gases, water-cooling of the quartz immediately behind the reaction place) gave no better results.

To summarise, it may be said that, according to our results, the methylene radical is far inferior to methyl and ethyl in stability, since where its formation is to be expected with some probability, carbon deposition occurs instead. Nevertheless, since our experimental method permits of free radicals being first detected some distance from the reaction place, *i.e.*, after many collisions with gas molecules and the tube walls, it is possible that free methylene might be detected with more refined methods. Indications of this are available in the work of Belchetz (*Trans. Faraday Soc.*, 1934, **30**, 170) and especially of Rice and Glasebrook (*J. Amer. Chem. Soc.*, 1933, **55**, 4329; 1934, **56**, 2381).

V. *Preparation of Free Benzyl.*—(i) *By thermal decomposition of tetrabenzyltin.* Free benzyl may be obtained by exactly the same procedure as free methyl and ethyl.* We decomposed

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* That the benzyl radical possesses a relatively high stability has already been concluded by Emde (*Helv. Chim. Acta*, 1932, **15**, 1330) from experiments on fission during hydrogenation.

tetrabenzyltin and allowed the products to react with mirrors of selenium, tellurium, and mercury. By reaction with selenium there resulted a yellowish substance of m. p. 75—76°. Since benzyl selenide melts at 45·5°, and dibenzyl diselenide at 90°, a mixture of both substances was apparently present. Indeed, by fractionation in a high vacuum, we could isolate an almost colourless substance containing selenium and melting sharply at 44—45°. This substance was therefore dibenzyl selenide, and the formation of the benzyl radical by the decomposition of tetrabenzyltin may be regarded as confirmed.

Gently-heated tellurium mirrors were also attacked by the decomposition products of tetrabenzyltin. A yellowish oil, in which tellurium was detected, and which after solidifying melted at 40°, was thereby produced. It was probably impure dibenzyl telluride (m. p. 53°), but could not be further purified on account of its minute quantity.

By reaction with mercury, the surface of which was continually renewed by distillation, a well-defined substance was formed in quantity sufficient to permit of fractionation in a high vacuum and its separation from dibenzyl. The m.p. was 115—117°, the recorded m.p. of dibenzyl-mercury being 117°. Mercury and dibenzyl were formed from the substance on heating, confirming the identification as dibenzylmercury. This reaction therefore also demonstrates the stability of free benzyl over a certain period. The possibility that dibenzylmercury might be formed by back diffusion of mercury into the zone of already decomposed tetrabenzyltin, against the gas stream, was disposed of by the fact that the compound is unstable at high temperatures, and that at low temperatures—up to 100°—mercury does not react with the tin aryl.

The yield of free benzyl by this reaction appears to be considerably less than that of free methyl and ethyl, since tellurium was only slowly attacked even when considerable amounts of the compound were decomposed. The greater proportion of free benzyl apparently passes directly into dibenzyl. In a 22-hour experiment, at dull red heat and 2 mm. pressure, 0·241 g. of dibenzyl was formed from 0·336 g. of tetrabenzyltin (87% yield).

(ii) *By thermal decomposition of dibenzyl ketone.* Since Rice (*J. Amer. Chem. Soc.*, 1932, **54**, 3529) obtained free methyl by the decomposition of acetone, we attempted to apply the same method to the preparation of free benzyl. We decomposed dibenzyl ketone in a red-hot silica tube, using hydrogen as carrier gas. Much dibenzyl was formed (identified by m. p., volatility, and smell). When a tellurium mirror heated at 80—100° was placed behind the decomposition place, it was attacked and a yellowish oil resulted. This was soluble in benzene, but the solution became turbid on standing, metallic tellurium separating. Owing to the very minute amounts of the oil available, no purification was attempted; since, however, it was a tellurium compound and not volatile at room temperature, it may be assumed from its mode of formation to be benzyl telluride.

(iii) *By reaction of benzyl chloride with sodium vapour.* When these two reactants diffused into one another, in a stream of helium, tellurium mirrors were attacked at a distance of 15 cm. from the reaction point. Blank experiments (passage of sodium vapour or benzyl chloride alone) left the mirrors unaltered. In the attack on the tellurium, a solid substance was formed which decomposed on warming in air, with separation of a grey deposit and an odour of benzaldehyde. It was thereby shown that free benzyl may be obtained in this manner also, but the method offered no advantages over the simpler methods described above.

The Life Period of Free Benzyl.—The reproducibility of results necessary for the determination of life periods was best achieved when the radical was obtained by method (ii), and allowed to react with tellurium mirrors at various distances. The formation of yellow, oily benzyl telluride of peculiar properties (see above) was taken as evidence of the production of free benzyl, since mere disappearance of the tellurium mirror could be produced likewise by hydrogen, methyl, or ethyl.

The experiments were made in a quartz tube of 0·5 cm. diameter, with a gas velocity of 20 m. per sec., at a pressure of 2 mm., using hydrogen as carrier gas. An action on gently heated tellurium mirrors was evident close (5 cm.) behind the decomposition point of the ketone. With a length of 25 cm. of unheated tube between the decomposition zone and the mirror, however, no free benzyl could be detected; but if the tube between decomposition place and mirror were heated to 200°, benzyl could still be detected at a distance of 25 cm.

After the life of free benzyl had thus qualitatively been shown to be considerable in a heated tube, we attempted to make the method quantitative. Tellurium, converted into dibenzyl telluride, was weighed as its dioxide after destruction of the organic matter. The results were as follows :

Expt. No.	Distance of mirror from decomposition point, cm.	Time of expt., t (hrs.).	Weight of TeO_2, g.	Activity, $A = g . 10^4/t$.
1	5	6·5	0·038	58
2	5	7·75	0·0185	24
3	25	14	0·0086	6
4	25	15·75	0·0111	7

The last column shows the weight of tellurium dioxide (g. $\times 10^4$) formed per hour, and so gives a measure of the activity A. Under constant conditions, the values of A in the pairs of experiments 1 and 2, 3 and 4, should be the same. The discrepancy between Expts. 1 and 2 is probably to be explained by variations in the temperature of the heating bath used to vaporise the ketone. Taking into account a streaming velocity of 15 m. per sec., and assuming a first-order reaction, the reaction constant K and half value period T may be calculated (from the mean of our experiments) as $K = 130$ and $T =$ approx. 6×10^{-3} sec.

It would be interesting to know how the half-value period of free benzyl compares with that of free methyl. Considering the inaccuracy of our experiments with free benzyl, and the numerous conditions upon which the life of the radicals depends (cf. Part V), we can only say that the life of benzyl in a cold tube is considerably shorter than, and in a heated tube is of the same order as, that of methyl. Corresponding to the view developed in Part V, it is probable that the more rapid decomposition in a cold tube is due to the higher accommodation coefficient. Only a direct comparison, however, of methyl and benzyl under identical conditions can decide the relative stabilities in a heated tube. Such an investigation would be, moreover, of particular interest in that we can regard benzyl, "monophenylmethyl," as a transition stage between the free methyl radical, comparatively stable in the gaseous state, and triphenylmethyl, stable in solution. To this question we hope to return later.

84. *The System* $CaCO_3$–$CaSO_4$–H_2O *at* 159° *to* 252°, *and the Effect of Additions of Sodium Salts.*

By L. M. CLARK and E. HUNTER.

A NORMAL boiler-feed water has in solution small quantities of sparingly soluble salts, in particular those of calcium. The concentration of the solution accompanying the production of steam is usually carried so far that solid salts are precipitated. If the salts are less soluble at high than at low temperatures, the rise in temperature alone may be sufficient to cause precipitation. The commonly occurring precipitates are calcium sulphate, which usually appears as a hard adherent scale on the heating surfaces, and calcium carbonate, which normally forms a sludge.

A thickening and adherent scale causes uneconomic working, and many attempts have been made to discover why some substances adhere to the tubes while others do not (for bibliography, see Partridge, "Formation and Properties of Boiler Scale," Univ. of Michigan Eng. Res. Bulletin No. 15, 1930). Since the mechanism of scale formation is not fully understood, the deposition of calcium sulphate as a sludge cannot be ensured and it is more profitable to consider methods of preventing its appearance as any kind of solid phase. The theory of the first successful method was investigated by Hall (*J. Ind. Eng. Chem.*, 1925, **17**, 283), who proposed to precipitate the calcium solely as carbonate sludge, by adjusting the relative amounts of carbonate and sulphate in the water. Theoretically, only calcium carbonate can be precipitated if the ratio of carbonate to sulphate exceeds the ratio of the solubility products of the two salts for the working temperature. It is quite clear that in practice only calcium carbonate will be precipitated if the CO_3/SO_4 ratio exceeds a certain magnitude, but this magnitude will only equal the ratio of the solubility products

if the solution behaves as an ideal one. In the absence of adequate solubility data, Hall estimated the critical CO_3/SO_4 ratios from the ratio of the solubility products at the various temperatures, that of the sulphate being calculated from the solubility of anhydrite at boiler temperatures, and that of the carbonate from an extrapolation of Kendall's measurements (*Phil. Mag.*, 1912, **23**, 958) of the solubility of calcite between 20° and 100°. The ratios thus obtained increased rapidly with rising temperature, and led to a carbonate content, at pressures above 250 lb./sq. inch, which would be so high as to cause risk of caustic embrittlement because of the production of a relatively high caustic alkalinity by decomposition of sodium carbonate.

It was thought, however, that lower ratios might suffice in practice, and work on the actual CO_3/SO_4 ratios in solutions of compositions similar to those of boiler waters was undertaken. The work has fallen into two divisions : The determination of the CO_3/SO_4 ratios for co-existence of the carbonate and sulphate (as calcite and anhydrite) in the system CaCO₃–CaSO₄–H₂O between 159° and 255° (1) without added compounds, and (2) with addition of sodium sulphate, chloride, or hydroxide.

EXPERIMENTAL.

A 2-litre Bergius rotary converter made of Firth's " H.R. Crown Max," designed for work at temperatures up to 400° and pressures up to 600 atm., was adapted to solubility work. The

FIG. 1.
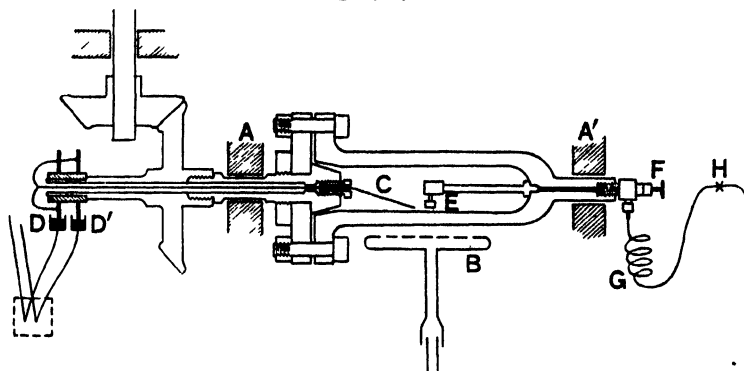
arrangement is shown in Fig. 1. The converter was held in the two bearings, A,A′ and could be rotated about this axis at a speed of 14 r.p.m. It was covered with a cowl, and heated by the gas burner B. The temperature was measured with a calibrated chromel–alumel couple within the sheath C. This sheath, made of stainless steel, was bent to within ¼″ of the inner bomb wall. The leads from the couple were connected to two insulated copper discs which dipped into the mercury troughs D,D′, from which chromel and alumel wires ran to cold junctions with copper. The wiring was arranged so that the E.M.F. could be measured with either a potentiometer or a recording instrument. By opening the valve F, samples for analysis could be withdrawn from the bomb through the filter E, which was fixed near the thermocouple top, about ¼″ from the bomb wall. Satisfactory filters were made by copper- or silver-plating small pieces of fine phosphor-bronze gauze until the interstices were small enough to act efficiently as filters (Manning, J., 1926, 1127).

A gas supply from a main served by a booster through a constant-pressure device was available, and there was no difficulty in regulating the supply with a fine-adjustment valve so that temperatures constant to ± 1·5° could be maintained.

In order to prevent evaporation, it was necessary to cool the sample before releasing it to atmospheric pressure. A cooling coil G, of copper capillary, was provided, fitted with a valve H. When a sample was to be taken, the rotation of the converter was stopped, and the cooling coil attached to the valve F. The coil was cooled with water and the valve opened. Rate of flow was governed by the valve H. As would be expected from the retrograde solubilities of calcium carbonate and calcium sulphate at high temperatures, cooling threw out no solid from solution. During the time taken for sampling, the temperature of the bomb as shown by the thermocouple was controlled in the normal way. Halting the stirring during sampling had no disturbing effect

on the equalisation of temperature throughout the bomb, for when rotation was recommenced no change in the thermocouple *E.M.F.* could be detected.

The bomb was charged in the following way. Equal weights of calcium carbonate (Hopkin and Williams; Ca, 39·45; CO_2, 59·93; SiO_2, 0·0019; Fe_2O_3, 0·0013%; Ba not detected) and anhydrous calcium sulphate (B.D.H.; Ca, 29·60; SO_4, 70·90%) were placed in the dry clean bomb, which was then closed, placed in position, and heated to about 80°. The weights of solid taken depended on the composition of solution added later, and varied between 1 g. of each for the system $CaCO_3$–$CaSO_4$–H_2O to 3 g. of each for solutions containing the higher concentrations of sodium sulphate or hydroxide. The bomb was evacuated through the valve F, and about 1300—1500 c.c. of distilled water or of a solution containing sodium salts in known concentration, previously boiled to remove dissolved gas and then cooled to 80°, were sucked in. By following this method, the risk of hydration of calcium sulphate was avoided. After closing the valve F, rotation of the bomb was started, and the temperature raised to the proper value. The stirring at constant temperature was continued for at least 24 hours. During the last 4 or 5 hours, particular care was taken with the hand control to keep the temperature steady to ± 1·5°. The first 100 c.c. of sample from the bomb were rejected, the following 1000 c.c. were run through a filter-paper into a calibrated flask and kept for analysis. A very slight discoloration of the filter-paper showed that some substance had been retained on it, but this deposit gave no sulphate reaction and no titration with acid, and its weight was negligible. The filtered sample was colourless and clear. The deposit probably came from the filter plates; it was more noticeable with copper than with silver filters. On opening the bomb soon after sampling, both calcite and anhydrite were always found as solid phases as pure white powders.

During the sampling period, measurements of the thermocouple *E.M.F.* were made frequently with the potentiometer. After sampling, the converter was again rotated, and the temperature measured to make sure that there had been no disturbance of the temperature equilibrium.

The sodium sulphate and sodium chloride solutions were made up from A.R. materials; the sodium hydroxide solutions were prepared by diluting standard solution of negligible carbonate content with carbon dioxide-free water.

Analysis.—(a) *System* $CaCO_3$–$CaSO_4$–H_2O. The samples were evaporated to dryness without boiling, on a hot-plate in weighed crystallising dishes of 8-cm. diameter, and the total solid determined by weighing the deposit after the dish had been heated to 150° for some hours, whereby the calcium sulphate was left as hemihydrate. It had been shown that these dishes exhibited no alkaline residue or change in weight after the evaporation in them of 1 l. of distilled water, so it was possible to determine the calcium carbonate content of a sample by titrating the residue with $N/10$-hydrochloric acid, using methyl-orange as indicator.* The residue was then digested with a small quantity of fairly concentrated hydrochloric acid until the calcium sulphate had dissolved, and the solution was then made up to 250 c.c. in a calibrated flask. Portions of this solution were taken for sulphate and calcium determinations, the former gravimetrically as barium sulphate, and the latter as oxalate, which was either converted into oxide and weighed, or determined by the permanganate method.

(b) *System* $CaCO_3$–$CaSO_4$–H_2O *with added salts.* Except for the equilibria reached from solutions containing added sodium hydroxide, the analytical methods were the same as those above, but silver dishes were used for the evaporation. In addition, determinations of the caustic alkalinity produced by hydrolysis were made on separate samples. The solutions containing added sodium hydroxide were analysed without evaporation to dryness, by determining the carbonate by the carbon dioxide evolution method and subtracting the equivalent carbonate from the total alkalinity to get the hydroxide content.

The samples were collected and their volumes measured at room temperature. Since the concentrations of dissolved substances are low, they can be expressed for all practical purposes as either g. per litre at room temperature or g. per 1000 g. of water.

Results.—The results are in Tables I—IV. Table I gives the equilibria in the system $CaCO_3$–$CaSO_4$–H_2O. The solubility of calcium carbonate is known to depend on the partial pressure of carbon dioxide over the solution. In the present case a closed vessel was used containing solution made up from carbon dioxide-free water and this pressure was presumably the very low pressure reached by the system itself through the decomposition pressure of calcium carbonate.

* The caustic alkalinity formed in the solution at 250° was measured. This proved to be very small, being only 7% of the carbonate content. Since this 7% at 250° is likely to be the maximum for the range studied and is no greater than the over-all experimental error, no account has been taken of it.

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TABLE I.

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Composition of Solutions in Equilibrium with Solid $CaSO_4$ *(Anhydrite) and* $CaCO_3$ *(Calcite) in the System* $CaCO_3$–$CaSO_4$–H_2O.

Temp.	Total solid ($CaSO_4,\frac{1}{2}H_2O$ + $CaCO_3$), g./1000 g. H_2O. By evaptn.	By analysis.	G./1000 g. H_2O. Ca.	SO_4.	CO_3.	Temp.	Total solid ($CaSO_4,\frac{1}{2}H_2O$ + $CaCO_3$), g./1000 g. H_2O. By evaptn.	By analysis.	G./1000 g. H_2O. Ca.	SO_4.	CO_3.
159°	0·210	0·208	0·058	0·131	0·006	206°	0·078	0·074	0·022	0·0358	0·012
159	0·212	0·208	0·059	0·130	0·007	206	0·072	0·070	—	0·0360	0·010
159	0·209	0·206	0·058	0·126	0·009	225	—	0·066	—	0·0302	0·012
159	0·208	0·209	0·060	0·128	0·012	225	0·048	0·048	—	0·0218	0·009
177	0·138	0·136	0·041	0·074	0·014	225	0·050	0·046	—	0·0214	0·008
179	0·139	0·139	0·041	0·079	0·012	241	0·040	0·036	—	0·0146	0·008
195	0·098	0·092	0·028	0·046	0·013	251	0·036	0·033	—	0·0132	0·008
195	0·092	0·091	—	0·050	0·009	252	0·030	0·030	—	0·0115	0·008
						252	0·032	0·031	—	0·0119	0·008

From Table I it will be seen that as the temperature rises the sulphate concentration falls, at first rapidly but later more slowly. The carbonate concentration at first rises slightly, but above about 200° it falls away. Over the whole of the temperature range the sulphate concentration is very much higher than the carbonate, so it is not surprising that the manner of the variation of sulphate concentration with temperature is much the same as it is in the two-component system $CaSO_4$–H_2O (Partridge, *op. cit.*, p. 43). On the other hand, the dissolved calcium carbonate is in the presence of a great excess of calcium ions (from the more soluble sulphate) and its behaviour as the temperature changes will be governed chiefly by the changes of the calcium concentration. Hence, at first as the temperature rises, the rapid fall in calcium sulphate concentration allows the calcium carbonate concentration to rise because of the great decrease in calcium-ion concentration. Later, the fall of calcium sulphate concentration with rise of temperature is not nearly so marked, and finally, as the metal-ion concentration becomes

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TABLE II.

Solubility of (Calcium Sulphate + Calcium Carbonate).

(a) *In sodium sulphate solutions.*

G./1000 g. H_2O.

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Temp.	Total solids. By evaptn.	By analysis.	Ca.	SO_4.	CO_3.	Na.	OH.	Na as Na_2SO_4 added.
159°	1·440	1·452	0·036	0·962	0·020	0·434	Nil	
159	1·467	1·477	0·040	0·983	0·020	0·434	Nil	
207	1·421	1·420	0·027	0·923	0·036	0·434	Nil	
206	1·374	1·365	0·016	0·880	0·035	0·434	Nil	1·339
225	1·358	1·371	0·010	0·872	0·055	0·434	Nil	
226	1·386	1·374	0·010	0·878	0·042	0·434	0·010	
259	1·351	1·338	0·0062	0·826	0·060	0·434	0·012	
257	1·369	1·379	0·0056	0·831	0·063	0·434	0·016	
159	2·803	2·822	0·038	1·886	0·030	0·868	Nil	
159	2·818	2·836	0·039	1·901	0·029	0·868	Trace	
207	2·748	2·758	0·014	1·821	0·053	0·868	0·002	2·678
207	2·733	2·736	0·013	1·800	0·055	0·868	Nil	
250	2·706	2·702	0·0067	1·741	0·072	0·868	0·014	
250	2·700	2·699	0·0070	1·738	0·074	0·868	0·012	
207	0·692	0·700	0·013	0·436	0·032	0·217	0·0042	
207	0·694	0·698	0·012	0·438	0·028	0·217	0·0030	0·670
250	0·672	0·663	0·0055	0·391	0·038	0·217	0·012	
250	0·676	0·661	0·0055	0·389	0·038	0·217	0·012	
250	0·276	0·262	0·0046	0·136	0·025	0·087	0·009	0·268
250	0·269	0·259	0·0050	0·133	0·024	0·087	0·010	

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(b) *In sodium carbonate solutions.*

</div>

Temp.	Total solids. By evaptn.	By analysis.	Ca.	SO_4.	CO_3.	Na.	OH.	Na as Na_2CO_3 added.
206	1·345	1·364	0·013	0·874	0·040	0·434	0·003	1·000
206	1·380	1·376	0·012	0·887	0·042	0·434	0·001	

steadier, the calcium carbonate concentration changes in the same way as it does in the system $CaCO_3$–H_2O, i.e., it decreases as the temperature rises.

Table I gives evidence that the solubility of the carbonate alone in water is retrograde. By converting the concentration into g.-mols./1000 g. H_2O, and taking the mean values of [Ca], [SO_4], and [CO_3] at each temperature, the solubility products [$Ca^{..}$][SO_4''] and [$Ca^{..}$][CO_3''] can be calculated, by using the relation [CO_3''] + [SO_4''] = [$Ca^{..}$] where no calcium concentrations are given, and assuming practically complete ionisation. The square roots of the solubility products give the approximate solubilities of the single salts in water. Both decrease as the temperature rises, throughout the temperature range.

The accuracy of Table I appears to be about ± 10% for [SO_4] and ± 20% for [CO_3].

Table II (a) shows the effect of the addition of sodium sulphate. It will be seen that at equilibrium the composition of the solutions can be expressed as having practically the original amount of sodium sulphate with very little sodium carbonate. This is in agreement with the results of two experiments in which sodium carbonate was added, shown in Table II (b), and for which it was found that the solution at equilibrium contained principally sodium sulphate produced by double decomposition of sodium carbonate with calcium sulphate. It will be seen that the caustic alkalinity of the solutions was small, but increased fairly rapidly with temperature above 220°.

Table III shows the results obtained with sodium chloride solutions, and also with solutions containing both added chloride and sulphate.

TABLE III.

Solubility of (Calcium Sulphate + Calcium Carbonate) in Sodium Chloride (and Sodium Sulphate) Solutions.

G./1000 g. H_2O.

Temp.	Total solids. By evaptn.	By analysis.	Ca.	SO₄.	CO₃.	Cl.	Na.	OH.	NaCl.
159°	2·593	2·552	0·102	0·231	0·009	1·342	0·868	Nil	
159	2·562	2·545	0·102	0·228	0·009	1·338	0·868	„	
206	2·373	2·338	0·039	0·073	0·011	1·346	0·868	0·0008	
206	2·367	2·329	0·039	0·072	0·011	1·338	0·868	0·0008	2·207
250	2·345	2·303	0·019	0·0257	0·010	1·377	0·868	0·0017	
250	2·347	2·267	0·020	0·0263	0·009	1·342	0·868	0·0026	
207	1·233	1·205	0·031	0·055	0·012	0·673	0·434	Trace	1·103
206	1·231	1·205	0·032	0·056	0·012	0·671	0·434	0·0005	
206	2·521	2·488	0·012	0·898	0·035	0·673	0·868	0·0021	1·103 *
206	2·480	2·482	0·013	0·895	0·036	0·669	0·868	0·0013	
207	3·613	3·578	0·014	0·881	0·024	1·349	1·302	0·0076	2·207 *
206	3·632	3·590	0·014	0·897	0·030	1·342	1·302	0·0047	

* With addition of Na_2SO_4 (Na equiv. to 1·339 g. Na_2SO_4/1000 g. H_2O).

TABLE IV.

Solubility of (Calcium Sulphate + Calcium Carbonate) in Sodium Hydroxide Solutions.

G./1000 g. H_2O.

Temp.	Total solid by analysis.	Ca.	SO₄.	CO₃.	OH.	Na.	Na as NaOH.
159°	2·114	0·074	0·691	0·010	0·471	0·868	
159	2·111	0·074	0·683	0·015	0·471	0·868	
207	1·950	0·025	0·583	0·012	0·462	0·868	1·509
206	1·965	0·025	0·591	0·012	0·469	0·868	
250	1·950	0·0110	0·580	0·011	0·481	0·868	
159	1·108	0·088	0·278	0·011	0·297	0·434	
159	1·105	0·088	0·274	0·008	0·301	0·434	
207	0·945	0·029	0·191	0·015	0·276	0·434	0·754
207	0·948	0·028	0·193	0·020	0·273	0·434	
250	0·900	0·0110	0·163	0·008	0·285	0·434	
250	0·900	0·0110	0·161	0·013	0·282	0·434	
159	0·651	0·075	0·197	0·008	0·154	0·217	
160	0·648	0·075	0·193	0·009	0·154	0·217	
207	0·500	0·031	0·087	0·013	0·152	0·217	0·377
207	0·501	0·030	0·086	0·016	0·152	0·217	
250	0·446	0·0140	0·049	0·0065	0·159	0·217	
250	0·444	0·0135	0·049	0·0041	0·160	0·217	
160	3·220	0·068	0·210	0·018	0·615	1·309	2·263

Table IV shows the effect of sodium hydroxide. It will be seen that at equilibrium the caustic alkalinity is appreciably less than that originally added, so that sodium sulphate has been formed. It has been suggested that the production of sulphate is due to double decomposition of caustic soda with calcium sulphate, with precipitation of calcium hydroxide. This would account for the fall in the caustic alkalinity, but microscopic examinations of the solid phases from the equilibria with caustic soda solutions gave no indications of the presence of lime.

In Tables II, III, and IV, the calcium concentrations appear to be accurate to about 5% and the sulphate concentrations to about 1%, while the carbonate concentrations are given probably to 7% in Tables II and III and to about 20% in Table IV.

DISCUSSION.

The CO_3/SO_4 ratios shown in Tables V, VI (a), (b), (c), and (d) have been calculated from values for carbonate and sulphate concentrations interpolated from smooth curves drawn through plots of the experimental data. The over-all accuracy is probably about 15%, although the data of Tables VI (a), (b), and (c) may be rather better than this.
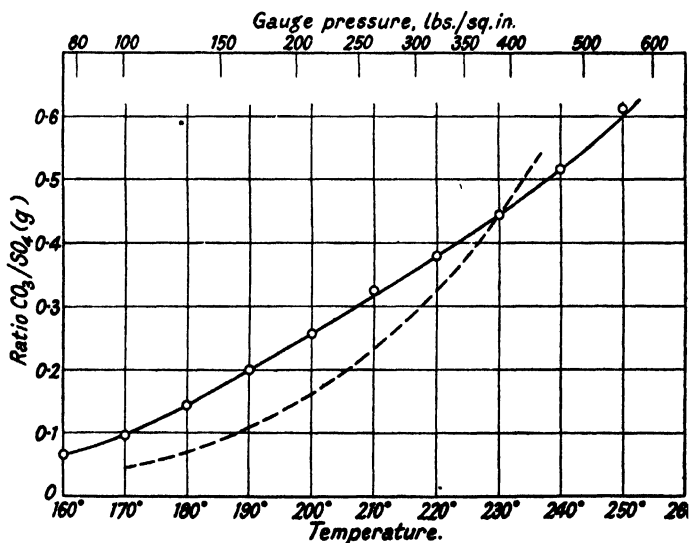
TABLE V.

Carbonate and Sulphate Concentrations and Carbonate/Sulphate Ratios in the System $CaCO_3$-$CaSO_4$-H_2O, *at* $160°$ *to* $250°$.

Temp.	Gauge, lbs./sq. in.	G./1000 g. H₂O. CO₃.	G./1000 g. H₂O. SO₄.	Ratio CO₃/SO₄ (g.).	Temp.	Gauge, lbs./sq. in.	G./1000 g. H₂O. CO₃.	G./1000 g. H₂O. SO₄.	Ratio CO₃/SO₄ (g.).
160°	75	0·0082	0·124	0·066	210°	262	0·0109	0·034	0·32
170	101	0·0092	0·094	0·098	220	322	0·0103	0·0272	0·38
180	131	0·0102	0·072	0·142	230	390	0·0095	0·0215	0·44
190	168	0·0109	0·055	0·198	240	470	0·0086	0·0167	0·51
200	211	0·0110	0·043	0·26	250	560	0·0077	0·0126	0·61

The ratios in the system $CaCO_3$-$CaSO_4$-H_2O between $160°$ and $250°$ are shown graphically in Fig. 2. The broken line is a plot of theoretical values calculated by Hall's method

FIG. 2.

In the figure: Gauge pressure, lbs./sq.in. (top axis: 80, 100, 150, 200, 250, 300, 350, 400, 500, 600); vertical axis: Ratio CO₃/SO₄ (g.) (0·1 to 0·6); horizontal axis: Temperature (160° to 260°).

(cited by Jones, "Fuel Economy Review," 1932). The agreement between the two is remarkable in view of the assumptions made in the calculation of the theoretical values. The theoretical values rise more rapidly with temperature than do the actual values in the three-component system, and exceed them above 230°. This difference is apparently due to Hall's use of Kendall's solubilities for calcium carbonate, which increase with rising temperature : actually the solubility decreases.

TABLE VI.

The Effect of Sodium Salts on the Carbonate and Sulphate Concentrations and CO_3/SO_4 Ratio by Additions to the System $CaCO_3$–$CaSO_4$–H_2O.

(Ratio = CO_3/SO_4 ratio in g. throughout.)

(a) *Sodium sulphate.*

Temp.	Gauge, lbs./sq. in.	CO₃.	SO₄.	Ratio.	CO₃.	SO₄.	Ratio.	CO₃.	SO₄.	Ratio.
		G./1000 g. H₂O.			G./1000 g. H₂O.			G./1000 g. H₂O.		
160°	75	0·0300	1·889	0·016	0·0203	0·970	0·021			
170	101	0·0338	1·873	0·018	0·0226	0·955	0·024			
180	131	0·0380	1·857	0·020	0·0252	0·940	0·027			
190	168	0·0427	1·840	0·023	0·0283	0·926	0·031			
200	211	0·0476	1·823	0·026	0·0317	0·911	0·035	0·0252	0·446	0·057
210	262	0·0523	1·806	0·029	0·0357	0·896	0·040	0·0277	0·432	0·064
220	322	0·0573	1·790	0·032	0·0402	0·882	0·046	0·0304	0·420	0·072
230	390	0·0625	1·774	0·035	0·0452	0·868	0·052	0·0332	0·409	0·081
240	470	0·0678	1·757	0·039	0·0506	0·853	0·059	0·0358	0·399	0·090
250	560	0·0734	1·740	0·042	0·0568	0·839	0·068	0·0383	0·390	0·098
260	665				0·0635	0·825	0·077			

Na equivalent to } 2·678 g. Na₂SO₄ per 1000 g. H₂O. | 1·339 g. Na₂SO₄ per 1000 g. H₂O. | 0·669 g. Na₂SO₄ per 1000 g. H₂O.

At 250° (gauge press. = 560 lbs./sq. in.), with Na equivalent to 0·268 g. Na₂SO₄/1000 g. H₂O: CO_3 = 0·0249, SO_4 = 0·134 g./1000 g. H₂O, ratio = 0·185.

(b) *Sodium sulphate + sodium chloride.*

206°	241	0·0359	0·897	0·040	0·0269	0·889	0·030

NaCl, g./1000 g. H₂O   1·103   2·207
Na₂SO₄, g./1000 g. H₂O   1·339   1·339

(c) *Sodium chloride* (2·207 g./1000 g. H₂O, except in last expt.).

Temp.	Gauge, lbs./sq. in.	CO₃.	SO₄.	Ratio.	Temp.	Gauge, lbs./sq. in.	CO₃.	SO₄.	Ratio.
		G./1000 g. H₂O.					G./1000 g. H₂O.		
160°	75	0·0092	0·226	0·041	220°	322	0·0107	0·052	0·206
170	101	0·0100	0·182	0·055	230	390	0·0104	0·042	0·248
180	131	0·0105	0·144	0·073	240	470	0·0100	0·033	0·303
190	168	0·0110	0·112	0·098	250	560	0·0095	0·026	0·365
200	211	0·0111	0·086	0·129	206 *	241	0·0118	0·056	0·211
210	262	0·0110	0·066	0·167					

* NaCl = 1·103 g./1000 g. H₂O.

(d) *Sodium hydroxide.*

| Temp.	Gauge, lbs./sq. in.	CO₃.	SO₄.	Ratio.	CO₃.	SO₄.	Ratio.	CO₃.	SO₄.	Ratio.
		G./1000 g. H₂O.			G./1000 g. H₂O.			G./1000 g. H₂O.		
160°	75	0·0103	0·685	0·015	0·0098	0·275	0·036	0·0087	0·195	0·045
170	101	0·0108	0·654	0·016	0·0125	0·255	0·049	0·0108	0·166	0·065
180	131	0·0111	0·628	0·018	0·0148	0·236	0·063	0·0126	0·140	0·090
190	168	0·0115	0·607	0·019	0·0165	0·218	0·076	0·0139	0·117	0·119
200	211	0·0116	0·593	0·020	0·0174	0·202	0·086	0·0145	0·097	0·149
210	262	0·0118	0·584	0·020	0·0174	0·188	0·092	0·0143	0·081	0·177
220	322	0·0117	0·580	0·020	0·0165	0·178	0·093	0·0132	0·068	0·193
230	390	0·0117	0·580	0·020	0·0151	0·170	0·089	0·0113	0·059	0·191
240	470	0·0115	0·580	0·020	0·0130	0·165	0·079	0·0086	0·052	0·165
250	560	0·0112	0·580	0·020	0·0104	0·162	0·064	0·0052	0·049	0·106

Na equivalent to } 1·509 g. NaOH per 1000 g. H₂O. | 0·754 g. NaOH per 1000 g. H₂O. | 0·377 g. NaOH per 1000 g. H₂O.

At 160° (gauge press. 75 lbs./sq. in.), with Na equivalent to 2·263 g. NaOH/1000 g. H₂O: CO_3 = 0·0184, SO_4 = 1·210 g./1000 g. H₂O, ratio = 0·015.

When sodium salts are added to the three-component system, it is not possible to represent fully the variation of the CO_3/SO_4 ratios by a graphical method. By making certain approximations, however, serviceable graphs can be constructed. By neglecting the small concentrations of sodium hydroxide present at equilibrium, the effect of sodium sulphate on the ratio can be expressed as in Fig. 3, where the ratio at 250°, 210°, and 160° is shown as a function of the total equilibrium SO_4 concentration, but reference should be

made to Table II for the precise compositions of the solutions. It will be seen at once that, when the solution contains appreciable quantities of sodium sulphate, neither Hall's theoretical values nor the ratios in the three-component system are even an approximation to the true state of affairs. Sodium sulphate lowers the ratio to a small fraction of that holding in the simple system at the same temperature, and also lowers the rate of increase

FIG 3.
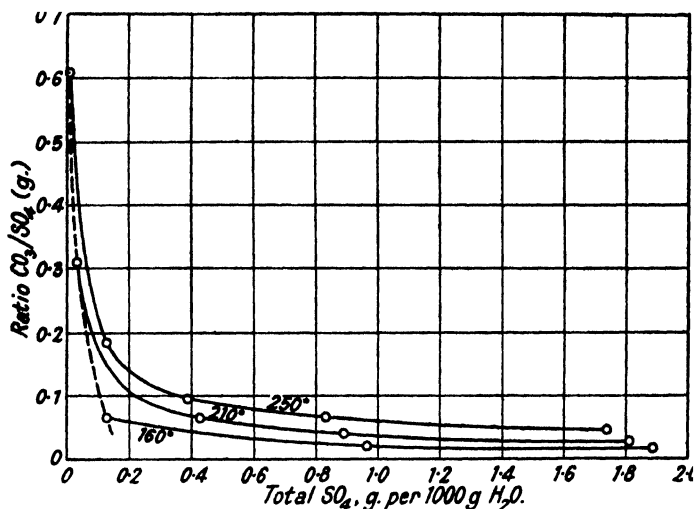
with temperature. It is clear, particularly at the higher temperatures, that the rate of lowering of the ratio with increasing SO_4 concentration decreases rapidly as the latter rises, so that at concentrations above 0·7 g. SO_4/1000 g. H_2O, the ratio, although very much less than that in the simple system, becomes roughly independent of the SO_4 concentration.
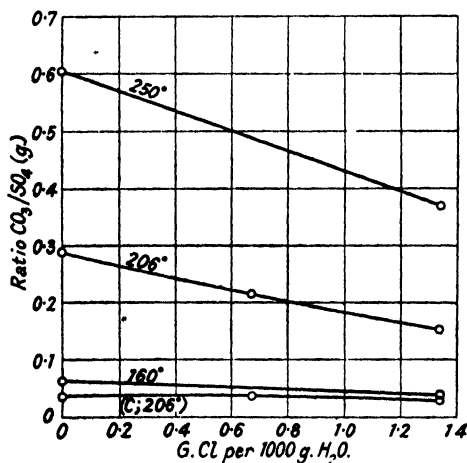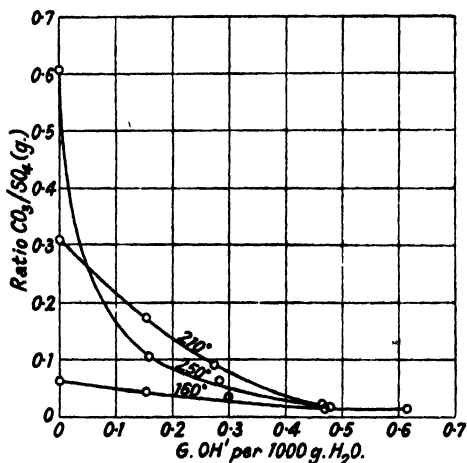
FIG. 4.   FIG. 5.

Fig. 4 shows the effect of sodium chloride at different temperatures. There is a lowering effect, but it is small compared to the effect of sodium sulphate, and the variation with temperature remains much the same as that in the simple system. In this figure is also shown (at *C*) the negligible effect on the CO_3/SO_4 ratio of the addition of sodium chloride to a solution containing 1·34 g. of added sodium sulphate per 1000 g. of H_2O, which has already lowered the ratio. From Table III it is seen that sodium chloride lowers the ratio by

increasing the calcium sulphate solubility, for the carbonate concentrations remain practically the same as in the simple system.

Fig. 5, which attempts to show the effect of sodium hydroxide, must be used only with reference to Table IV, which gives the full analyses of the solutions, since there is the complication that addition of the alkali brings about a great increase in the sodium sulphate concentration. The possibility of the production of solid calcium hydroxide from the caustic soda at the expense of calcium sulphate must also be kept in mind, particularly with regard to boiler practice, where the calcium sulphate is limited in quantity. In the present experimental work, large quantities of both calcium carbonate and sulphate were undoubtedly present as solid phases at equilibrium, so that it is possible to give the true CO_3/SO_4 ratio for solutions of the compositions given in Table IV. Due allowance must be made for the increased sulphate concentration which accompanies the caustic soda. Thus, Fig. 5 shows the ratio to be 0·019 at 250° with a concentration of 0·48 g. of OH' per 1000 g. of H_2O, but the sulphate concentration associated with this, 0·58 g./1000 g. H_2O, would alone suffice to reduce the ratio to 0·08 from its value of 0·6 in the simple system. For the reasons which have been given, it is difficult to assess the quantitative effect of hydroxide alone on the CO_3/SO_4 ratio; all that can be said is that it appears to lower it more than does sodium chloride. In practice an OH concentration unaccompanied by an appreciable SO_4 concentration is not likely to be encountered.

These conclusions are further supported by Straub's recent work, (" The Cause and Prevention of Calcium Sulphate Scale in Steam Boilers," Bulletin No. 261, 1933, Engineering Experiment Station, University of Illinois). Examination of his results, however, shows that he has not made a systematic determination of the CO_3/SO_4 ratios for the co-existence of the two solid phases calcium carbonate and calcium sulphate, since he took no steps to ensure that *both* solid phases were present together in the equilibria he studied. His results give the compositions of various solutions in equilibrium with either one or the other, but do not show the *minimum* CO_3/SO_4 ratios for the prevention of calcium sulphate precipitation.

SUMMARY.

Carbonate/sulphate ratios have been determined in solutions in equilibrium with the co-existing solid phases calcium carbonate (calcite) and calcium sulphate (anhydrite).

In the system $CaCO_3$–$CaSO_4$–H_2O between 159° and 252°, the ratios found by experiment increase less rapidly with temperature than do those calculated by previous workers, and above 230° are lower than these calculated figures.

The effect on the CO_3/SO_4 ratio of low concentrations of dissolved sodium salts has also been studied. The ratio is reduced greatly by sodium sulphate, and much less effectively by sodium chloride. When sodium hydroxide is added to the three-component system, an appreciable concentration of sodium sulphate is found at equilibrium; the greatly lowered CO_3/SO_4 ratio in these alkaline solutions is principally brought about by the sodium sulphate formed, but is in part due to sodium hydroxide.

85. *The Chemistry of Insects. Part I. The Wax of the Felted Beech Coccus.*

By B. K. BLOUNT.

THE insect *Cryptococcus fagi,* Barensprung, lives on the trunks and larger branches of beech trees, which it often ultimately kills, and is to be reckoned among the more serious of the British insect pests. It secretes a protective felted mass of wax fibres, from which its

popular name, the felted beech coccus, is derived. A knowledge of the nature of this wax not only is of interest from the biogenetic point of view, but also may provide a clue to the best method of destroying the insects.

Since repeated crystallisation caused but little alteration in its melting point, the wax is probably a single substance or a mixture of closely related compounds. On hydrolysis, approximately equal amounts of an acid and of an alcohol were formed, analyses and melting points of which indicated their identity as " cerotic " acid, $C_{26}H_{52}O_2$, and " ceryl " alcohol, $C_{26}H_{54}O$, respectively. Confirmation of this was obtained by oxidising the alcohol with chromic acid, whereby it was converted into an acid closely similar to that formed by the hydrolysis of the wax.

It has recently been shown (Piper, Chibnall, and Williams, *Biochem. J.*, 1934, 28, 2175; Chibnall, Piper, Pollard, Williams, and Sahai, *ibid.*, p. 2189) that in general the acids and alcohols derived from natural waxes are mixtures; and in particular that " cerotic " acid and " ceryl " alcohol from these sources are mixtures having an approximate mean chain length of 26 carbon atoms.

By applying the data contained in the first paper mentioned above to the products isolated from *Cryptococcus fagi* wax, an insight has been gained into its approximate composition. The alcoholic component gave an acetate, m. p. 58·7—59·1°, indicating a mean chain length of 25·6. The m. p. of the free alcohol (77·5—78·0°) showed that a mixture of this mean composition must be at least ternary : and both this m. p. and that of the derived acid are satisfied by a mixture of about 80% of the C_{26} compound with 20% of a mixture of the C_{24} and C_{28} compounds, the former predominating. The acid component, m. p. 81·1—82·0°, gives an ethyl ester, m. p. 60·4—60·8°, and is therefore a ternary mixture containing some 70—80% of the C_{26} acid, together with 30—20% of the C_{24} and C_{28} acids.

The wax of *Cryptococcus fagi* consists, therefore, of a mixture of esters of the C_{24}, C_{26}, and C_{28} acids and alcohols, in which the C_{26} compounds largely predominate.

The suggestion of Chibnall, Latner, Williams, and Ayre (*Biochem. J.*, 1934, 28, 313) that a second hydrolysis with sodium ethoxide is essential if the alcoholic constituent is to be obtained pure, was fully confirmed.

EXPERIMENTAL.

Isolation of the Wax.—The felted mixture of insects and wax (96 g.) was scraped off the trunks of affected beech trees, and the wax dissolved out by several extractions with hot chloroform. The filtered extracts were united and evaporated to 250 c.c., and an equal volume of hot ethyl alcohol added. Crystallisation began at once, and, after cooling, the wax was collected, washed with alcohol, and dried in the air. Yield 38 g., m. p. 80·2—81·3°. For purification it was crystallised several times from chloroform (charcoal being used in the first crystallisation), and finally from chloroform–alcohol, the latter being in excess. It separated from this mixture in colourless shining plates, m. p. 81·0—81·5°, particularly suitable for filtering and drying (Found : C, 81·5; H, 13·8. $C_{52}H_{104}O_2$ requires C, 82·0; H, 13·8%).

Hydrolysis of the Wax.—The purified wax (7 g.), caustic potash (7 g.), and ethyl alcohol (150 c.c.) were refluxed together for 17 hours. Calcium chloride (10 g.) in alcohol (70 c.c.) was then added, and the heating continued for a further 2 hours. The calcium salts were filtered off hot, washed with boiling alcohol, again boiled with alcohol and filtered off hot, and finally boiled with chloroform, filtered, and repeatedly washed with hot chloroform. After drying they were decomposed by boiling for an hour with acetic acid, the solution being filtered, and poured into water. The precipitated acid was crystallised three times from acetic acid (charcoal), from which it separated in feather-like aggregates of long colourless plates, m. p. 81·1—82·0° (Found : C, 79·0, 78·8; H, 13·4, 13·5. Calc. for $C_{26}H_{52}O_2$: C, 78·7; H, 13·2%). The ethyl ester melted at 60·4—60·8°.

The alcoholic filtrates from the calcium salts deposited the crystalline alcohol on cooling. It melted over a considerable range, and could not be purified by repeated crystallisation (Found : C, 80·9, 80·7; H, 14·3, 13·9%). It was therefore further hydrolysed by refluxing with a solution of sodium (2 g.) in alcohol (75 c.c.) for 20 hours. After precipitation of the calcium salts the alcohol was isolated as before and crystallised from acetone (250 c.c.) (charcoal), cooling only to about 25°. The alcohol (2·35 g.) crystallised in rosettes of long glistening

plates, and, after two further crystallisations from the same solvent, melted at 77·5—78·0° (Found : C, 81·5; H, 14·2. Calc. for $C_{26}H_{54}O$: C, 81·6; H, 14·2%). The acetate, prepared by boiling the alcohol with pure acetic anhydride for 4 hours, melted at 58·7—59·1°.

Oxidation of the Alcohol to the Related Acid.—A solution of the alcohol (191 mg.) in acetic acid (30 c.c., purified by distillation over chromic acid) was treated at the b. p. during 10 minutes with a solution of potassium dichromate (98 mg.) in 90% acetic acid (10 c.c.), and constantly shaken. After being kept near the b. p. for 1 hour, the mixture was allowed to cool, and the solid collected. Since the m. p. was not sharp, the acid was converted into its calcium salt, which was purified by extraction with hot alcohol and chloroform. The regenerated acid, after crystallisation from acetic acid, melted at 81·5—82·3°, and the mixture with an equal amount of the acid prepared by the hydrolysis of the wax had m. p. 81·2—82·0°.

The author wishes to thank Professor Chibnall for advance proofs of the papers referred to in the text, and for his advice in the application of the data contained therein to these results ; also the Royal Commissioners of the Exhibition of 1851 for a Senior Studentship.

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86. *The Energetics of Catalysis. Part IV. The Influence of Deactivation by Heat Treatment on the Value of the Activation Energy.*

By Edward B. Maxted and Charles H. Moon.

In earlier papers of this series, the evidence for the energetic uniformity of the catalysing elements of a metallic surface, such as that of platinum, has been examined from various standpoints, including the influence of progressive inactivation by means of a poison (J., 1933, 502) ; and it has now been considered of interest to study the effect on the activation energy of partial deactivation by heat treatment. While the nature of the deactivation process involved differs essentially from inhibition of activity by the progressive and obstructive occupation by a poison of elements normally free for catalysis, the application of the present work to the question of energetic uniformity is based largely on considerations which have already been discussed in the above paper, particularly if any active points or peak areas which exist in the surface be viewed as extra-lattice projections differing among themselves in nature and in order of stability in such a way that the process of stabilisation by heat treatment might be expected to affect certain of these preferentially.

Two heterogeneous reactions, of distinct types, *viz.*, the decomposition of hydrogen peroxide and the hydrogenation of crotonic acid in the liquid phase, have, in this case, been chosen for study, the activation energies with a platinum catalyst at various stages of deactivation by heat treatment being determined in the usual way by means of the temperature coefficient of the reaction velocity.

This ratio of the reaction velocities at two given temperatures, and consequently the calculated value of the activation energy, was found in each case not to vary appreciably with the state of deactivation of the platinum, although different values were, as would be expected, obtained for the two different reactions. It may be noted that this constancy is in agreement with the observations of Pease and Harris (*J. Amer. Chem. Soc.*, 1927, 49, 2503) for the hydrogenation of ethylene in the gas phase in the presence of a copper catalyst, supported on a ceramic base, before and after sintering.

Experimental.

The standard platinum black used was prepared by Mond, Ramsay, and Shields's method (*Phil. Trans.*, 1895, *A*, 186, 657) by the reduction of chloroplatinic acid with an alkaline solution of sodium formate, the same preparation of platinum being employed for all measurements within a given series. From this main stock smaller portions were taken, as required, for partial deactivation by heat treatment at various temperatures, the sintering being carried out in a small Pyrex vessel contained in an electrically heated enclosure or, for lower temperatures, in an oil- or nitre-bath.

The general technique for the determination of the reaction velocity was, in the main, as previously described (J., 1921, 119, 225; 1934, 26). For the hydrogenation of crotonic acid, a solution of this compound in glacial acetic acid, to which the platinum was added, was treated with hydrogen in a shaking pipette, under controlled conditions, in a thermostat. For the decomposition of hydrogen peroxide, a shaking method, involving the measurement of the oxygen evolved (J., 1922, 121, 1760), was used in place of following the progress of the reaction by titration, as had been done in the work involving deactivation by poisoning (J., 1933, 502).

Decomposition of Hydrogen Peroxide.—For each measurement, 50 c.c. of a 0·16N-solution of hydrogen peroxide were placed in the reaction pipette and kept in the thermostat for a sufficient time to attain the required temperature. 0·025 G. of platinum, taken from a stock in a given state of inactivation and preheated to reaction temperature in 5 c.c. of water, was now added, and the shaking mechanism put into operation. The reaction follows, as is well-known, a course of the first order.

The results obtained are summarised in Table I, in which k_{10} and k_{30} are the unimolecular velocity constants, at 10° and 30°, respectively, with specimens of platinum taken from stocks previously sintered for 30 mins. at the temperatures indicated. The 20° temperature difference not only gave a convenient (approximately 3-fold) rise of reaction, but also—with the catalyst first in its highly active unsintered state and finally in the relatively inactive form produced by sintering at 400°—approximately covered the range between the limits of velocity which could conveniently be read off in the gas burettes attached to the shaker.

TABLE I.

Temp. of previous heat treatment of catalyst.	Activity, expressed as % of original activity.	k_{10}.	k_{30}.	k_{30}/k_{10}.
(Unsintered)	100	0·23	0·634	2·76
250°	23	0·052	0·142	2·73
300	7·8	0·018	0·050	2·77
350	4·4	0·0101	0·0275	2·72
400	2·6	0·00607	0·0170	2·80
			Average	2·76

It will be seen that, in the course of progressive deactivation by heat treatment involving an ultimate decrease in the activity of the platinum to less than 3% of its original activity, the value of the ratio k_{30}/k_{10} remains approximately constant, the observed deviation from the mean being of the order of 2%, which represents the degree of agreement of duplicate activity measurements. The mean value of the ratio, *viz.*, 2·76, corresponds with an activation energy of about 8,700 cals. for the temperature range 10—30°.

It was considered of interest, further, to compare the value of the activation energy given for the present, relatively dense specimens of platinum black with those which had previously been obtained for the same reaction (*loc. cit.*) with a far more finely divided form of the metal prepared by another method. Since, in the previous work, a somewhat lower temperature range had been employed, the temperature coefficient of the present platinum was determined in somewhat greater detail down to 0°. This was done with a stock which had previously been sintered at 250°, the following variation being observed :

Temp.	0°	10°	15°	20°	25°	30°
k	0·023	0·052	0·065	0·084	0·111	0·142

From this, the average activation energy, calculated in the usual way, is 10,800 cals. between 0° and 15°, compared with about 11,000 cals. found for the same temperature interval with the relatively finely divided platinum in the previous work, the agreement between 0° and 25°, although not quite so satisfactory, being within 7%. In any case, the degree of concordance between the values given by the two widely differing preparations of platinum is striking. The activation energies calculated on the basis of the simple Arrhenius equation are probably, in the case of heterogeneous catalytic reactions of the types studied in the present paper, apparent energies only; and an attempt is being made elsewhere to analyse the factors contributing to the apparent temperature coefficient, with special reference to the variation of the apparent critical energy with the temperature.

Hydrogenation of Crotonic Acid.—The standard charge taken for hydrogenation consisted of 10 c.c. of a N-solution of crotonic acid in acetic acid, the same stock being used throughout

the whole work. This, together with the required quantity of platinum, was placed in a closed pipette, provided with a stoppered side tube to facilitate the introduction of the charge, and hydrogenated by shaking in an apparatus of the usual type (*Trans. Faraday Soc.*, 1917, **13**, 36).

Preliminary experiments were carried out to determine the effect, under the conditions employed, of a variation in the quantity of platinum on the temperature coefficient, since it was considered necessary, first of all, to make sure that the mere diminution of the speed of hydrogenation brought in itself no change in the temperature coefficient. The results of measurements with varying amounts of platinum are summarised in Table II, in which k_{15} and k_{35} are the velocities of the hydrogenation reaction, which follows a course of approximately zero order, at 15° and 35°, respectively, the velocity being expressed in c.c. of hydrogen absorbed per minute.

<p style="text-align:center">TABLE II.</p>

Pt, g.	k_{15}.	k_{35}.	k_{35}/k_{15}.	Pt, g.	k_{15}.	k_{35}.	k_{35}/k_{15}.
0·025	3·3	7·7	2·34	0·1	17·1	40·0	2·34
0·05	7·8	18·2	2·34	0·1	17·4	40·6	2·33

As was expected, this mere decrease in the amount of platinum had no effect on the temperature coefficient.

In the first series of measurements of the effect of heat treatment, a freshly prepared stock of platinum (Platinum A) was employed. In choosing a suitable temperature range, reaction temperatures below 10° were precluded by the solidification of the acetic acid solution used, but temperatures of 10° and 30° were, with 0·05 g. of this platinum, found to give hydrogenation velocities of convenient relative magnitude throughout the series. The general effect of sintering this platinum on the reaction velocities at the two temperatures in question and on the ratio of these velocities is shown in Table III.

<p style="text-align:center">TABLE III.</p>

Temp. of previous heat treatment of catalyst.	Activity, expressed as % of original activity.	k_{10}.	k_{30}.	k_{30}/k_{10}.
(Unsintered)	100	4·85	12·0	2·5
200°	81	3·9	9·9	2·5
250	56	2·7	6·4	2·4
300	35	1·5	3·6	2·4
350	19	0·95	2·4	2·5

The result is similar to that observed in the decomposition of hydrogen peroxide, in that the reduction of activity by heat treatment exerts no measurable effect on the temperature coefficient. It will be noted, further, that the ratio of the velocities at 30° and 10° differs slightly from the ratio at 35° and 15° (Table II); and, on calculating the corresponding activation energies, these are again found to decrease slightly as the temperature is increased, *viz.*, from 7,600 cals. between 30° and 10° to 7,500 cals. in the somewhat higher range.

A further series of measurements was carried out with a second stock of platinum (Platinum B), which was not specially prepared but was available from other work, and had been prepared by the fusion of chloroplatinic acid with sodium nitrate, followed by the reduction with hydrogen of the platinum oxide thus produced (Voorhees and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 1397). This platinum had, before being taken for the present purpose, been employed for a considerable time for the adsorption of ethylene and had, in the course of its use, apparently become stabilised, since it was not so sensitive to heat treatment as Platinum A; indeed, for some reason, its activity was increased by exposure to moderate sintering temperatures. As before, however, deactivation by exposure even to a relatively high temperature had, as far as could be seen, no effect on the temperature coefficient and consequently on the apparent activation energy of the hydrogenation reaction.

The results obtained with 0·05 g. of this catalyst in various states of deactivation are collected in Table IV.

Again, the ratio of the reaction velocities at the two temperatures is unaffected; moreover, the mean value of k_{35}/k_{15}, *viz.*, 2·35, corresponding with an apparent activation energy of 7,500 cals., agrees well with that calculated from Table II.

As a slight variation in the method of deactivation, the length of the sintering period was now varied, once more, however, without appreciably affecting the velocity ratio. In the

TABLE IV.

Temp. of previous heat treatment of catalyst.	k_{15}.	k_{25}.	k_{25}/k_{15}.	Temp. of previous heat treatment of catalyst.	k_{15}.	k_{25}.	k_{25}/k_{15}.
200°	11·4	27·0	2·4	400°	14·0	32·0	2·3
250	12·2	28·8	2·4	450	9·5	22·8	2·4
300	13·4	30·8	2·3	500	3·7	8·8	2·4
350	13·5	31·5	2·3	550	3·45	7·9	2·3

TABLE V.

Time of previous heat treatment of platinum, mins.	k_{15}.	k_{25}.	k_{25}/k_{15}.	Time of previous heat treatment of platinum, mins.	k_{15}.	k_{25}.	k_{25}/k_{15}.
(Unsintered)	8·8	20·8	2·4	120	6·0	13·9	2·3
30	9·5	21·4	2·3	180	5·1	12·0	2·4
60	6·8	15·3	2·3				

measurements summarised in Table V, 0·05 g. of Platinum B and a uniform sintering temperature of 450° were employed.

The activation energy calculated from the above ratio is identical with that derived from Tables II and IV.

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87. *The Formation of Organo-metalloidal Compounds by Micro-organisms. Part III. Methylated Alkyl- and Dialkyl-arsines.*

By FREDERICK CHALLENGER and LOUIS ELLIS.

THE formation of dimethylethylarsine by the growth of *Penicillium brevicaule* (*Scopulariopsis brevicaulis*) Saccardo on sterile bread crumbs containing sodium ethylarsonate, EtAsO(ONa)$_2$, has been described (J., 1933, 95). This type of reaction, involving both methylation and reduction, has been further studied. By addition of (a) diethylarsinic acid, Et$_2$AsO·OH (Wigren, *Annalen*, 1924, **437**, 285; Grischkewitsch-Trochimowski, *Rocz. Chem.*, 1928, **8**, 423), (b) *n*-propylarsonic acid, and (c) allylarsonic acid, CH$_2$:CH·CH$_2$·AsO(OH)$_2$ (Quick and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 807) to similar cultures of the same strain (A) of the mould (J., 1933, 95) in concentrations varying from 0·2 to 0·5%, mixed methylated arsines are produced. These have been removed in a sterile air stream, and absorbed in suitable reagents.

Methyldiethylarsine is obtained from (a) and converted into (1) the *dimercurichloride* and (2) *hydroxymethyldiethylarsonium picrate*. Similarly (b) gives dimethyl-*n*-propylarsine, which has been identified as (3) the *dimercurichloride*, (4) *benzyldimethyl*-n-*propylarsonium picrate*, and (5) *hydroxydimethyl*-n-*propylarsonium picrate*.

In an analogous manner (c) gives rise to *dimethylallylarsine*, which has been characterised as (6) the *dimercurichloride* and (7) *benzyldimethylallylarsonium picrate*. Absorption in nitric acid is in this case unsuitable as indicated by preliminary experiments with the synthetic arsine. All the above compounds have been analysed [(4) excepted] and in all cases compared as regards m. p. and mixed m. p. with analysed specimens obtained from the synthetic arsines.

Growth of the mould on bread or on aqueous media containing potassium antimonyl tartrate with or without glucose gave no odour of an alkyl stibine. This is in agreement with the negative results obtained by Knaffl-Lenz (*Arch. exp. Path. Pharm.*, 1913, **72**, 224), Tiegs (*Kleine Mitth. Wasserversorg.*, 1925, **1**, 51), and Smith and Cameron [*Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 401].

EXPERIMENTAL.

P. brevicaule Saccardo (*Baarn Strain A*) *and Diethylarsinic Acid.*—Five 1-l. flasks, each containing 150 g. of bread, were inoculated and incubated for 4 days at 30° and at room temperature

for 1 day, and 25 c.c. of a sterile 1% solution of diethylarsinic acid added to each. Concentration = approx. 0·2%. The flasks were connected in two parallel sets of 3 in series and 2 in series, and the volatile matter passed into one bottle containing Biginelli's solution (mercuric chloride in hydrochloric acid; J., 1933, 96). A trace of precipitate formed in the solution after 3 days, but increased very slowly and after 27 days the small amount was removed. It had m. p. 202° (decomp.) and the same on recrystallisation. There was not sufficient for a second recrystallisation and it may have contained a trace of mercuric chloride. It did not depress the m. p. of synthetic methyldiethylarsine dimercurichloride, m. p. 196—198°, decomp. 201° (Found : C, 8·6; H, 1·8. Calc. for $C_5H_{13}Cl_4AsHg_2$: C, 8·7; H, 1·9%).

The poor yield of arsine from diethylarsinic acid is possibly due to the toxic action of this acid on the mould. Earlier experiments with sodium cacodylate (J., 1933, 98) gave much less trimethylarsine than was obtained with sodium methylarsonate.

Two experiments in which (a) disodium diethylarsinate and (b) monopotassium diethylarsinate were present in the medium in concentrations of about 0·4% were also made. In (a) after 60 days no garlic odour and no precipitate were obtained. In (b) after 93 days the amount of dimercurichloride obtained (2 deposits) was only sufficient for a determination of the m. p.'s, 199—200° and 200—202°.

Hydroxymethyldiethylarsonium picrate, $OH \cdot AsMeEt_2 \cdot O \cdot C_6H_2(NO_2)_3$.—Absorption of the mould gas in nitric acid, evaporation, and precipitation with sodium picrate gave yellow crystals, m. p. 128—130°, and 134—135° in admixture with authentic synthetic picrate (m. p. 134—135°) (Found : C, 33·15; H, 4·4. Calc. : C, 33·6; H, 4·1%).

P. brevicaule Sacc. *and* n-*Propylarsonic Acid.*—*Dimethyl*-n-*propylarsine dimercurichloride*, $AsMe_2Pr,2HgCl_2$. Four 1-l. flasks (150 g. of bread) were inoculated and incubated at 30° for 4 days and at room temperature for 2 days. To each flask were added 25 c.c. of a sterile solution made from n-propylarsonic acid (2·23 g.), potassium bicarbonate (1·33 g.), and water (125 c.c.), giving a concentration of about 0·3% of the monopotassium salt in each flask. A garlic odour was detected after 2 days and was still perceptible after 12 weeks. A deposit formed in the Biginelli's solution after 3 days weighed 0·09 g. on the 23rd day, sintered at 187°, melted at 195°, and decomposed, evolving gas, at 200°. It was mixed with 0·11 g. of an exactly similar product obtained in a duplicate experiment and recrystallised (as in the case of all mercurichlorides prepared in this research) from hot water containing a little mercuric chloride; m. p. 195°, decomp. 200°. It did not depress the m. p. of synthetic dimethyl-n-propylarsine dimercurichloride, m. p. 195°, decomp. 200° (Found : C, 8·5; H, 1·8; Cl, 19·9. Calc. for $C_5H_{13}Cl_4AsHg_2$: C, 8·7; H, 1·9; Cl, 20·5%).

Benzyldimethyl-n-*propylarsonium picrate*, $CH_2Ph \cdot AsMe_2Pr \cdot O \cdot C_6H_2(NO_2)_3$. From the 23rd to the 51st day of the experiment the arsenical gas was absorbed in alcoholic benzyl chloride. The resulting quaternary salt was converted into the picrate in the usual way (J., 1933, 99). This was mixed with a further quantity obtained in a fresh experiment of 69 days' duration. The m. p. was 108—110° and 113—114° on recrystallisation from hot water. The product, which was obtained in yield barely sufficient for analysis, did not depress the m. p. (113—114°) of synthetic benzyldimethyl-n-propylarsonium picrate.

Hydroxydimethyl-n-*propylarsonium picrate*, $OH \cdot AsMe_2Pr \cdot O \cdot C_6H_2(NO_2)_3$. From the 51st to the 86th day nitric acid (d 1·4) was used as absorbent. Evaporation then gave a trace of semi-solid residue, which with aqueous sodium picrate gave a precipitate, m. p. 136—139°, and 142—143·5° after two recrystallisations from water. In admixture with synthetic hydroxydimethyl-n-propylarsonium picrate (m. p. 143—144°) the m. p. was 142—143·5° (Found : C, 33·8; H, 4·2; N, 10·5. Calc. : C, 33·6; H, 4·1; N, 10·7%).

P. brevicaule Saccardo *and Allylarsonic Acid.*—Four 1-l. flasks (150 g. of bread). Incubation 4 days at 30°, 1 day at room temperature. To each were added 25 c.c. of a solution of allylarsonic acid (5 g., m. p. 128—129°. Quick and Adams give m. p. 128—129°) and potassium bicarbonate (3 g.) in water (250 c.c.).

Concentration in the bread = 0·35%. There was a slight odour in 2 days and a slight deposit in Biginelli's solution in 3 days. After 21 days 0·1 g. of precipitate was removed, m. p. 200° (decomp.). With sodium hydroxide it turned yellow and then black, evolving an intense odour, the usual behaviour of an aliphatic arsine mercurichloride (J., 1933, 99).

Absorption in fresh Biginelli's solution then gave deposits of 0·1 g., 0·1 g., 0·35 g., and 0·09 g. after 9, 8, 8, and 12 days. Total, 0·74 g. in 58 days. Yield, about 9%. The combined precipitates had m. p. 209° (decomp.) before and after crystallisation in the usual way. In admixture with synthetic dimethylallylarsine dimercurichloride (m. p. 209° decomp.) the m. p. was unaffected. The m. p.'s of both the synthetic and the mould mercurichlorides depend on the rate

of heating, variations of as much as 6° being observed with the same specimen on different occasions (Found : C, 8·1; H, 1·7; Cl, 20·9. Calc. for $C_9H_{11}Cl_4AsHg_2$: C, 8·7; H, 1·6; Cl, 20·6%).

Absorption of the mould gas in benzyl chloride gave a quaternary salt, which was converted into *benzyldimethylallylarsonium picrate*, $CH_2Ph·AsMe_2(C_3H_5)·O·C_6H_2(NO_3)_3$, m. p. 96—97° after recrystallisation, not depressing the m. p. of the synthetic picrate, 96—97° (Found : C, 46·2; H, 4·2; N, 8·9. $C_{18}H_{20}O_7N_3As$ requires C, 46·4; H, 4·3; N, 9·0%). It is clear from these results that the mould does not reduce the double linkage in the allyl group.

Preparation of Reference Compounds from Synthetic Arsines.—Dimethyl-n-propylarsine, b. p. 21°/22 mm., was prepared by the method of Jones (J., 1932, 2284), who gives b. p. 27°/17 mm. With excess of Biginelli's solution it gave the *dimercurichloride*, m. p. 195°, decomp. 200°, after recrystallisation (Found : C, 8·5; H, 1·7; Cl, 20·3. $C_5H_{13}Cl_4AsHg_2$ requires C, 8·7; H, 1·9; Cl, 20·5%).

Dimethyl-n-propylarsine monomercurichloride, AsMe₂Pr,HgCl₂, m. p. 126—128°, was obtained from the calculated quantities of the ingredients in dilute hydrochloric acid or in alcoholic solution. In the former case the reaction was gradual (Found : C, 14·2; H, 3·3; Cl, 16·9. $C_5H_{13}Cl_2AsHg$ requires C, 14·3; H, 3·1; Cl, 16·9%).

Benzyldimethyl-n-propylarsonium picrate was obtained from equal volumes (1 c.c.) of the arsine and benzyl chloride. The arsonium chloride was deliquescent and gave a picrate, m. p. 113—114° on recrystallisation (Found : C, 46·3; H, 4·6; picric acid, as nitron picrate, 49·3. $C_{18}H_{22}O_7N_3As$ requires C, 46·3; H, 4·75; picric acid, 49·0%).

Hydroxydimethyl-n-propylarsonium picrate. Addition of a few drops of nitric acid to the arsine caused immediate reaction and white fumes. Addition of water and evaporation gave an oily hydroxynitrate which did not crystallise. The *picrate* had m. p. 142—144°, and 143—144° on recrystallisation from hot water (Found : C, 33·3; H, 4·1; picric acid, 58·2. $C_{11}H_{16}O_8N_3As$ requires C, 33·6; H, 4·1; picric acid, 58·3%).

Methyldiethylarsine. The arsine was prepared following the general procedure of Jones (*loc. cit.*) from methyldi-iodoarsine (50 g.), ethyl bromide (60 g.), and magnesium (14 g.). It boiled at 112—114° in an atmosphere of carbon dioxide. Yield, 10 g. Cahours (*Annalen*, 1862, **122**, 220) gave no b. p.

Excess of Biginelli's solution gave the *dimercurichloride*, AsMeEt₂,2HgCl₂, which on recrystallisation had m. p. 196—198° and decomp. 201°. It was also obtained by slow passage of air over an *iso*amyl ether solution of the arsine into Biginelli's solution (see J., 1933, 97) (Found : C, 8·8; H, 2·2; Cl, 20·1. $C_5H_{13}Cl_4AsHg_2$ requires C, 8·7; H, 1·9; Cl, 20·5%).

Methyldiethylarsine monomercurichloride was formed (rather slowly) from the calculated amounts of its ingredients in dilute hydrochloric acid or alcoholic solution; m. p. 153—154° (Found : C, 14·3; H, 3·2; Cl, 17·2. $C_5H_{13}Cl_2AsHg$ requires C, 14·3; H, 3·1; Cl, 16·9%).

Benzylmethyldiethylarsonium picrate, $CH_2Ph·AsMeEt_2·O·C_6H_2(NO_3)_3$, was obtained as in similar cases; m. p. 85—86° (Found : C, 46·4; H, 4·9; picric acid, 48·8. $C_{18}H_{22}O_7N_3As$ requires C, 46·3; H, 4·75; picric acid, 49·0%).

Benzylmethyldiethylarsonium styphnate, $CH_2Ph·AsMeEt_2·O·C_6H(OH)(NO_2)_3$. The arsonium chloride was treated with a solution of sodium carbonate (anhydrous, 3·7 g.), and styphnic acid (8·5 g.) in water (250 c.c.). After recrystallisation from hot water the precipitate melted at 89—90° (Found : C, 44·7; H, 4·5. $C_{18}H_{22}O_8N_3As$ requires C, 44·8; H, 4·6%. The ingredients are united in equimolecular proportion).

Hydroxymethyldiethylarsonium picrate. The arsine (0·5 c.c.) was slowly added to dilute nitric acid (5 c.c.), but remained undissolved. Addition of the concentrated acid gave thick white fumes and a clear solution. This on evaporation left a colourless hydroxynitrate which did not solidify. The corresponding *picrate*, recrystallised from hot water, had m. p. 134—135° (Found : C, 33·6; H, 4·2; picric acid, 58·35. $C_{11}H_{16}O_8N_3As$ requires C, 33·6; H, 4·1; picric acid, 58·3%).

Dimethylallylarsine was prepared in the usual manner. The solution of allylmagnesium bromide was obtained by the method of Gilman and McGlumphy (*Bull. Soc. chim.*, 1928, **43**, 1322) as modified slightly by Shoemaker and Boord (*J. Amer. Chem. Soc.*, 1931, **53**, 1508). The arsine was fractionated in carbon dioxide at ordinary pressure. It boils at 108—110°, is colourless, has a very penetrating odour, and is spontaneously inflammable on filter-paper in air. Arsenic was determined by the iodometric method of Ewins (J., 1916, **109**, 1356) (Found : As, 51·1, 51·6. $C_5H_{11}As$ requires As, 51·3%).

Dehn and Wilcox (*Amer. Chem. J.*, 1906, **35**, 20) describe this arsine as a light yellow liquid, b. p. about 160°, obtained from methylarsine and allyl iodide in a sealed tube. They give no analysis of it or of the corresponding methiodide.

The *dimercurichloride*, m. p. 208—209° (decomp.), was obtained with Biginelli's solution (Found : C, 8·5; H, 1·4; Cl, 20·4. $C_6H_{11}Cl_4AsHg_2$ requires C, 8·7; H, 1·6; Cl, 20·6%).

Dimethylallylarsine monomercurichloride, $C_5H_6 \cdot AsMe_2, HgCl_2$, prepared from its ingredients in alcohol or dilute hydrochloric acid, has m. p. 120—121° (Found : C, 14·3; H, 2·8; Cl, 17·3. $C_5H_{11}Cl_2AsHg$ requires C, 14·4; H, 2·7; Cl, 17·0%).

Benzyldimethylallylarsonium picrate was prepared in the usual way, the arsine and benzyl chloride being mixed in an atmosphere of carbon dioxide. The closed box described by Dyke and Jones (J., 1930, 1923) was used in this and several similar reactions. The picrate melts at 96—97° after crystallisation from hot water (Found : C, 46·3; H, 4·4; picric acid, 49·3. $C_{18}H_{20}O_7N_3As$ requires C, 46·4; H, 4·3; picric acid, 49·2%).

Trimethylallylarsonium iodide, $C_3H_5 \cdot AsMe_3 \cdot I$. Dimethylallylarsine (2 c.c.) was added to excess of methyl iodide in a carbon dioxide atmosphere. The mixture solidified in a few minutes; it was dissolved in methyl alcohol and concentrated to half its volume on the steam-bath, and the arsonium salt precipitated by ether. A second crystallisation from methyl alcohol–ether gave white crystals, m. p. 184—186° (Found : I, 44·4. $C_6H_{14}IAs$ requires I, 44·1%).

Atmospheric Oxidation of Aliphatic Tertiary Arsines.—Dimethylallylarsine. During the preparation of the arsine its ethereal solution was evaporated. The recovered ether, kept in a loosely corked vessel for some time, evaporated, leaving a residue. Solution in alcohol and addition of ether gave a white solid, m. p. 195—196°. In admixture with cacodylic acid (m. p. 195—197°) the m. p. of the latter was unchanged.

The filtrate with alcoholic picric acid gave a yellow precipitate, m. p. 155—157°. One re-crystallisation from water gave the constant m. p. of 159—160° (Found : C, 33·6; H, 3·8; N, 10·7. $C_{11}H_{14}O_8N_3As$ requires C, 33·75; H, 3·6; N, 10·7%). The compound was therefore *hydroxydimethylallylarsonium picrate*. It could not be prepared from the arsine and nitric acid, since almost complete oxidation occurred (see p. 396).

Trimethylarsine. A similar behaviour was exhibited by trimethylarsine, which, with limited access of air, gave after 6 weeks a white powder, from which by an exactly similar process cacodylic acid (m. p. 197—199°, and 198—200° in admixture with an authentic specimen, m. p. 198—200°) and hydroxytrimethylarsonium picrate, m. p. 218—219° (J., 1933, 100), were isolated.

(Trimethylarsine is best prepared by the action of methylmagnesium iodide on dimethyl-iodoarsine rather than on arsenic trichloride. Reduction to elementary arsenic is thereby avoided and a much better yield is obtained.)

Triethylarsine with limited access of air gives diethylarsinic acid (Friedrich and Marvel, *J. Amer. Chem. Soc.*, 1930, 52, 376).

Triethylarsine monomercurichloride, m. p. 161—162°, has been prepared from its ingredients in alcoholic solution (Found : C, 16·2; H, 3·4. Calc. for $C_6H_{15}Cl_2AsHg$: C, 16·6; H, 3·5%) Attempts to obtain a pure dimercurichloride by using excess of Biginelli's solution or of alcoholic mercuric chloride failed. The product melted at 130—140° and from its behaviour on crystallisation appeared to be a mixture.

Grischkewitsch-Trochimowski describes a compound $AsEt_3, HgCl_2$, m. p. 163—164°, and also mentions a monomercurichloride of trimethylarsine, $AsMe_3, HgCl_2$, decomposing at 256° (*Rocz. Chem.*, 1928, 8, 423; 1926, 6, 798), but gives no analysis in the latter case. The dimercurichloride of trimethylarsine melts at 264° (decomp.), and the monomercurichloride at 224—226° (J , 1933, 96, 97).

Derivatives of Trimethylstibine.—An ethereal solution of the stibine was prepared by Hibbert's method (*Ber.*, 1906, 39, 160). The ethereal reaction mixture after treatment with ammonium chloride solution was distilled in carbon dioxide, giving an ethereal solution of the stibine.

A portion of this solution was treated with benzyl chloride and the resulting *benzyltrimethyl-stibonium picrate* isolated and recrystallised from hot water; m. p. 183—185° (Found : C, 39·3; H, 3·7; N, 8·7. $C_{16}H_{18}O_7N_3Sb$ requires C, 39·5; H, 3·7; N, 8·65%).

P. brevicaule and Potassium Antimonyl Tartrate.—To a culture of the mould on 50 g. of sterile bread in a 750 c.c. flask were added 25 c.c. of a sterile 5% tartar emetic solution. Aspiration through Biginelli's solution gave no precipitate after 30 days, and no odour was observed at any time.

Growth of P. brevicaule *on Liquid Media containing Potassium Antimonyl Tartrate.*—To two groups of three flasks containing 100 c.c. of Czapek–Dox medium (J., 1934, 65; inorganic salts only) 1 g., 2 g., and 3 g. of tartar emetic were added. Glucose (2 g.) was added to one group, and the sterilised media inoculated. Growth began in the glucose flasks after 7, in the others after 10 days. No odour was detected during 33 days and the cultures were then left for 9 months.

The flask containing 2% glucose and 3% tartar emetic was then examined. The filtered medium was free from antimony, hydrogen sulphide giving only a faint yellow colour. The washed mycelium contained opaque shining crystalline particles (observed in all six flasks), doubtless antimony trioxide, since on washing with tartaric acid large quantities of antimony were dissolved. The mould, therefore, consumes the tartrate and throws antimony trioxide out of solution.

Similar results were obtained with 250 c.c. Czapek–Dox medium (inorganic salts only) containing 12·5 g. of tartar emetic. Failure to detect trimethylstibine under these conditions might possibly be due to its ease of oxidation. On addition of 10 c.c. of the ethereal solution (see above) to a flask containing 50 g. of dry bread crumbs, the odour of the stibine, which was at first very pronounced, completely disappeared in 35 minutes. An attempt to isolate trimethyl-stibine oxide as the corresponding picrate from a liquid culture of the mould containing tartar emetic was unsuccessful.

88. *Studies in Pyrolysis. Part I. The Pyrolysis of Derivatives of α-Acetoxypropionic Acid, and Related Substances.*

By ROBERT BURNS, D. TREVOR JONES, and PATRICK D. RITCHIE.

A NEW pyrolytic process has been devised, of very general application, whereby derivatives of α-hydroxy-acids may be converted smoothly into the corresponding Δ^α-unsaturated acid derivatives. The difficulty of effecting such a synthesis by *direct* dehydration of α-hydroxy-acid derivatives is well known, though a derivative of a β-hydroxy-acid very readily yields the desired unsaturated compound on dehydration by any of the usual methods. It has now been found, however, that the elements of water may readily be removed *indirectly* from the α-hydroxy-compounds, by acetylating the hydroxy-group and submitting the acetoxy-compound to pyrolysis at 400—600° : acetic acid is eliminated smoothly, leaving the desired olefinic compound :
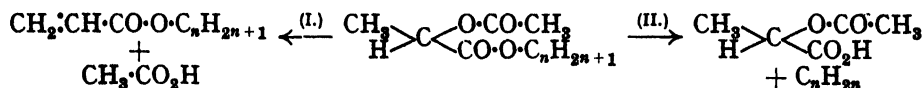
$$\begin{matrix} CH_3 \\ R \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} O \cdot CO \cdot CH_3 \\ X \end{matrix} \longrightarrow CH_3 \cdot CO_2H + CH_2 \!:\! CRX$$
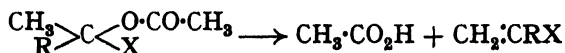
(R = H or alkyl; X = a negative acidic radical, such as $CO \cdot O \cdot CH_3$ or CN)

The same result may be achieved by esterifying the α-hydroxy-group with agents other than acetylating agents—*e.g.*, benzoyl chloride, carbonyl chloride, or methyl hydrogen phthalate—and pyrolysing the product.

The results obtained where R = hydrogen are now described; others will be described in subsequent papers.

Pyrolysis of Acetylated α-Hydroxy-esters.—Two different mechanisms are involved in the pyrolysis of an acetylated α-hydroxy-ester. For example, the alkyl α-acetoxypropionates undergo pyrolytic fission thus :

$$\begin{matrix} CH_2\!:\!CH \cdot CO \cdot O \cdot C_nH_{2n+1} \\ + \\ CH_3 \cdot CO_2H \end{matrix} \xleftarrow{\text{(I.)}} \begin{matrix} CH_3 \\ H \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} O \cdot CO \cdot CH_3 \\ CO \cdot O \cdot C_nH_{2n+1} \end{matrix} \xrightarrow{\text{(II.)}} \begin{matrix} CH_3 \\ H \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} O \cdot CO \cdot CH_3 \\ CO_2H \end{matrix} + C_nH_{2n}$$

Decomposition of methyl α-acetoxypropionate ($n = 1$) follows route (I) exclusively up to about 500°. The well-known thermostability of methyl esters in general prevents fission of olefin from the alkyl group, and methyl acrylate can be obtained in yields of 90%, calculated on the methyl α-acetoxypropionate actually " cracked." For ethyl α-acetoxy-propionate ($n = 2$), both routes are followed simultaneously. At about 450°, only 20% of the total ester is " cracked " per run, and ethyl acrylate is obtained *via* route (I) in yields of 76%. Route (II) becomes important, however, above 450°; the yield of ethyl acrylate falls off rapidly, ethylene is eliminated from the alkyl group, and acetaldehyde is obtained

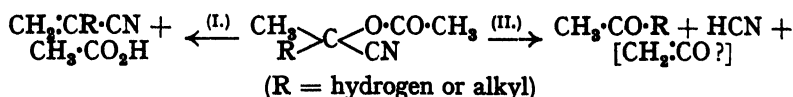in quantity, probably owing to secondary pyrolysis of the resulting α-acetoxypropionic acid, thus :

$$CH_3 >\!\!C\!\!< {}^{O \cdot CO \cdot CH_3}_{CO_2H} \longrightarrow CH_3 \cdot CHO + CO + CH_3 \cdot CO_2H$$
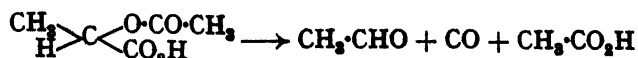
(cf. Hurd, " The Pyrolysis of Carbon Compounds," New York, 1929, p. 535).

With n-*butyl* α-*acetoxypropionate* ($n = 4$) the effective limit for the synthesis of alkyl acrylates by this method has been passed. Route (II) predominates markedly, a large amount of acetaldehyde is produced, the waste gases consist largely of butylene and carbon monoxide, and only 15—25% yields of n-*butyl acrylate* are obtained.

Benzyl α-*acetoxypropionate* apparently pyrolysed exclusively according to route (I), as was to be expected in view of the known thermostability of the benzyl radical, and *benzyl acrylate* was obtained in yields of about 75%.

Pyrolysis of Acetylated α-*Hydroxy-nitriles.*—The pyrolytic decomposition of acetylated cyanohydrins (α-hydroxy-nitriles) involves two different mechanisms :

$$\begin{array}{c} CH_2\!:\!CR\cdot CN + \\ CH_3\cdot CO_2H \end{array} \xleftarrow{\text{(I.)}} {}^{CH_3}_{R}\!\!>\!\!C\!\!<{}^{O\cdot CO\cdot CH_3}_{CN} \xrightarrow{\text{(II.)}} \begin{array}{c} CH_3\cdot CO\cdot R + HCN + \\ [CH_2\!:\!CO\,?] \end{array}$$

(R = hydrogen or alkyl)

Route (I) predominates up to about 450°, but small amounts of hydrogen cyanide and $CH_3 \cdot CO \cdot R$ always accompany the nitrile $CH_2\!:\!CR\cdot CN$. Keten itself was not identified; presumably it at once united with the free acetic acid, from route (I), forming small quantities of acetic anhydride.

Exactly parallel phenomena were observed on pyrolysis of 1-*cyanocyclohexyl acetate* :
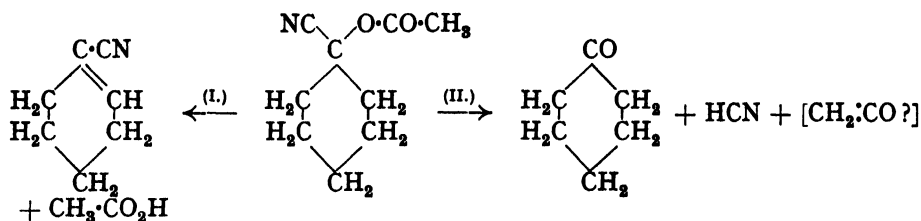
Scope of the Reaction.—The above type of pyrolysis into an acid and the olefinic compound $CH_2\!:\!CRX$ is general in application, and holds for α-hydroxy-compounds esterified with monobasic acids other than acetic, such as benzoic acid. When, for example, ethyl lactate is esterified with methyl hydrogen phthalate, *methyl* α-*carbethoxyethyl phthalate* is obtained, which breaks down at 550° into methyl alcohol, phthalic anhydride, and ethyl acrylate. Since Nagel and Abelsdorff (*Wiss. Veröff. Siemens-Konz.*, 1926, **5**, 193) have shown that an alkyl hydrogen phthalate is formed as an intermediate stage in the analogous pyrolysis of various dialkyl phthalates, it is probable that pyrolysis occurs here in two successive stages :
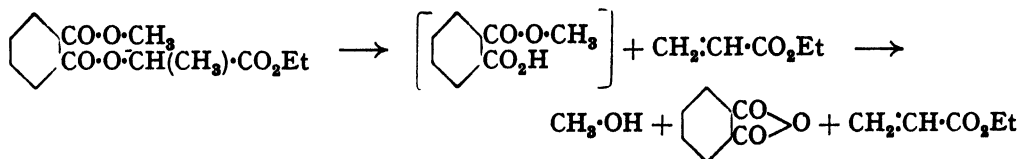
In this case, the yields of ethyl acrylate are poor (about 40%), owing to secondary fission of ethylene from the α-carbethoxy-group, as described previously.

Since dehydration of a hydroxy-acid derivative is rendered easier when the hydroxy-group is transferred from the α- to the β-position (with reference to the negative acidic group), it became of interest to determine whether pyrolytic deacetylations of the type now described were subject to analogous conditions—that is, whether they occurred more readily when the acetoxy-group was transferred from the α- to the β-position. This at first sight seemed probable, for, although no such comparable pair of reactions appears in

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the literature, several cases have been recorded in which the indirect dehydration of a β- or a γ-hydroxy-acid derivative has been effected by pyrolytic deacetylation of its acetate, either at the boiling point of the latter, or at a temperature much lower than those found necessary in the present work. For example, Kohler (*Amer. Chem. J.*, 1898, **20**, 683) has observed the following pyrolysis at only 185° :

$$CH_3 \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot SO_3K \longrightarrow CH_3 \cdot CO_2H + CH_2 \cdot CH \cdot SO_3K$$
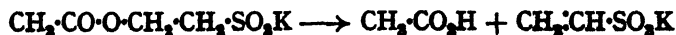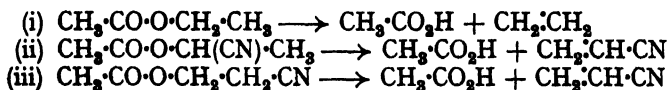
Similarly, the so-called " acetyl lævulinic acid " breaks down on distillation, even at 200—230 mm., in the following way (Thiele, Tischbein, and Lossow, *Annalen*, 1901, **319**, 184; Bredt, *ibid.*, 1890, **256**, 314) :

$$CH_3 \cdot \underset{\underset{O}{\underline{\quad\quad}}}{\overset{O \cdot CO \cdot CH_3}{C}} \cdot CH_2 \cdot CH_2 \cdot CO \longrightarrow CH_3 \cdot CO_2H + CH_3 \cdot \underset{\underset{O}{\underline{\quad\quad}}}{C} : CH \cdot CH_2 \cdot CO$$
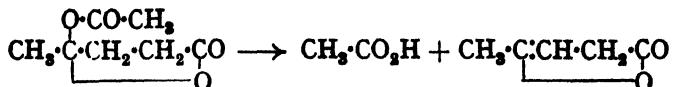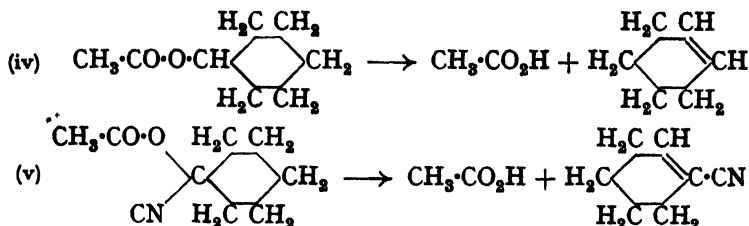
In interpreting such results, however, it should not be overlooked that ease of pyrolysis may here be expected to be affected by two independent factors, (1) the relative positions of the negative acidic group and the carbon atom to which the acetoxy-group is attached, and (2) the degree of substitution at this carbon atom. Just as tertiary carbinols undergo pyrolytic dehydration more readily, in general, than primary and secondary, so it has been found that their acetates undergo pyrolysis at relatively low temperatures (Menschutkin, *Ber.*, 1882, **15**, 2512). It is, therefore, probable that the ready pyrolysis of " acetyl lævulinic acid " is due more to the tertiary condition of the γ-carbon atom which bears the acetoxy-group than to the remoteness of the latter from the CO·O⁻ group.

This reservation should be borne in mind in considering the following three pyrolyses, which were carried out under strictly comparable conditions, ethyl acetate being included for comparison with the α- and the β-cyanoethyl acetate :

(i) $CH_3 \cdot CO \cdot O \cdot CH_2 \cdot CH_3 \longrightarrow CH_3 \cdot CO_2H + CH_2 : CH_2$
(ii) $CH_3 \cdot CO \cdot O \cdot CH(CN) \cdot CH_3 \longrightarrow CH_3 \cdot CO_2H + CH_2 : CH \cdot CN$
(iii) $CH_3 \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot CN \longrightarrow CH_3 \cdot CO_2H + CH_2 : CH \cdot CN$

Reaction (iii) proceeded more readily than (ii), and (ii) slightly more readily than (i). Here, therefore, the ease of pyrolysis increases when the acetoxy-group is transferred from the α- to the β- position—a not unexpected result when the analogous dehydration of the parent α- and β-hydroxy-compounds is remembered. The concurrent transformation of the carbon atom which carries the acetoxy-group from the secondary to the primary state is here probably of subordinate importance.

The introduction of a cyano-group into the alkyl radical of ethyl acetate appears to increase the ease of pyrolysis slightly : and in this connection it is interesting to note that reaction (v) proceeds slightly more readily that (iv) :

(iv) $CH_3 \cdot CO \cdot O \cdot CH \Big\langle \begin{smallmatrix} H_2C \enspace CH_2 \\ \\ H_2C \enspace CH_2 \end{smallmatrix} \Big\rangle CH_2 \longrightarrow CH_3 \cdot CO_2H + H_2C \Big\langle \begin{smallmatrix} H_2C \enspace CH \\ \\ H_2C \enspace CH_2 \end{smallmatrix} \Big\rangle CH$

(v) $\underset{CN}{\overset{CH_3 \cdot CO \cdot O}{>}} C \Big\langle \begin{smallmatrix} H_2C \enspace CH_2 \\ \\ H_2C \enspace CH_2 \end{smallmatrix} \Big\rangle CH_2 \longrightarrow CH_3 \cdot CO_2H + H_2C \Big\langle \begin{smallmatrix} H_2C \enspace CH \\ \\ H_2C \enspace CH_2 \end{smallmatrix} \Big\rangle C \cdot CN$

The table summarises these results.

The apparatus used entirely obviated the objectionable charring and strong discoloration produced in most modes of organic pyrolysis. By keeping the temperature and the time of contact well below the optima for complete " cracking," secondary reactions were largely, and in some cases entirely, suppressed; after recovery of the " uncracked " material, yields of the desired unsaturated compound approaching the theoretical (calculated in all cases on the material destroyed) could often be obtained by working up the crude product suitably.

Acetate.	Temp.	Rate, c.c. per min.	Weight, g., used.	Weight, g., recovered.	Ester recovered, %.	Olefin, %., calc. on ester destroyed.
Ethyl †	340—360°	4·5	118	117	99—100	Not measured
	440—460	4·5	136	130	95	,, ,,
	550—560	4·5	143	126	70	,, ,,
α-Cyanoethyl........	350—370	5	111	109·5	96—97	Not measured.
	440—460	5	132	128	92	,, ,,
	540—550	4·5	113	108	64 *	ca. 95
β-Cyanoethyl........	350—370	4	116	113	80 *	Not measured
	450—460	6	199	194	70 *	,, ,,
	540—560	4·5	220	211	12 *	,, ,,
cycloHexyl	350—360	4	66	65	98—99	Negligible
	460—470	4	117	116	66	>90
	550—560	4·5	115	111	1	94
1-Cyanocyclohexyl	340—350	8	86	83	89	ca. 80
	440—450	8	122	113	54	81
	540—550	5	134	128	<1	80

* Figures only approximate : error of about ±3%.

† The pyrolysis of ethyl acetate was described by Oppenheimer and Precht (*Ber.*, 1876, **9**, 325), but no temperatures were recorded.

EXPERIMENTAL.

The apparatus was essentially as follows : A 40″ iron tube, 1¼″ in diameter, was lined with Pyrex glass, and supported inside a vertical cylindrical electric furnace. The lower (exit) end was drawn out into a 6″ nozzle, ¼″ in diameter : a similar nozzle was fitted to the upper (entrance) end by a gas-tight threaded joint. The liquid was dropped vertically into the tube from a 300-c.c. tap-funnel, connected to the nozzle by a glass adapter and stout rubber tubing and fitted with the usual device for equalising the pressures above and below the liquid. The adapter carried an inlet tube by which a gentle current of an inert gas (carbon dioxide or nitrogen) could be passed through the whole system. A sulphuric acid bubbler, and a T-piece safety valve dipping below a 12″ head of water, were provided for the entering gas stream, and also a trap, just before the entrance nozzle, to catch any volatile product of pyrolysis which might tend to distil back. The temperature of the gas stream was registered by a platinum–iridium thermocouple, placed in the centre of the pyrolysis tube, and connected to a direct-reading galvanometer by wires passing out of the exit nozzle through slits in the stopper connecting it to the receiver. This was a well-cooled flask; any uncondensed vapour was led through a condenser to a second receiver. The exit gases were passed, where necessary, through wash-bottles of bromine, etc.

The pyrolysis tube was loosely packed with quartz chips, the free space being about 200 c.c. This packing offered a very large heated contact-surface to the vapour, and was used in all the experiments described in this series, unless otherwise stated. (A 30″ helix of strip aluminium proved almost equally efficient : pyrolysis also occurred, though to a markedly less extent, without any packing.)

Except where described in detail, the crude product was worked up by collecting three fairly sharply boiling fractions—the unsaturated compound, acetic acid, and uncracked material. The intermediate fractions were washed with brine till free from acetic acid, and the insoluble portion added to the appropriate main fraction, which was then further fractionated. In all cases where a polymerisable liquid was being distilled, a little quinol or sulphur was added to minimise the risk of heat-polymerisation.

Methyl α-Acetoxypropionate.—Preparation. Methyl lactate was treated with acetic anhydride and a little concentrated sulphuric acid. The mixture was distilled in a vacuum : pure methyl α-acetoxypropionate was obtained in 79—82% yield, and a further quantity of slightly crude product (*ca.* 13%) by extracting the intermediate fractions with brine. Freudenberg and Rhino (*Ber.*, 1924, **57**, 1552) give b. p. 168—170° for the pure ester. We have found b. p. 171·5—172°/760 mm., 76—77°/12 mm., n_D^{20} 1·4111, and d_4^{20} 1·088.

Pyrolysis. 327 G. of the ester were run into the pyrolysis tube at 470—485°, at the rate of 5 c.c./min. 313 G. of liquid were collected, which yielded 68 g. of almost pure, recovered acetoxy-ester and 122 g. of slightly crude methyl acrylate, b. p. mostly 80—83° (88% yield, calculated on the methyl α-acetoxy-propionate destroyed). The latter on refractionation yielded pure methyl acrylate, b. p. 79—80°/740 mm. (Found : C, 55·7; H, 6·9. Calc. : C, 55·8; H, 7·0%). When this was heated at 100° in presence of 1% of benzoyl peroxide, it polymerised with vigorous

frothing, giving a pale yellow, tough, rubbery mass, which did not harden after 20 hours' heating.

Ethyl α-Acetoxypropionate.—Preparation. This was prepared from ethyl lactate, acetic anhydride, and concentrated sulphuric acid in yields of 87—91%.

Pyrolysis. 126 G. of the pure ester (b. p. 177—178°) were run at the rate of 5 g./min. into the pyrolysis tube at 450°. 119 G. of liquid were collected, which yielded 100 g. of unchanged acetoxy-ester and 10·5 g. of crude ethyl acrylate (76% yield). The latter was washed, dried, and refractionated, yielding ethyl acrylate, b. p. 96—98°/744 mm. (Found : C, 59·6; H, 7·7. Calc. : C, 60·0; H, 8·0%). Heating at 100° with 1% of benzoyl peroxide produced a soft, pale yellow polymeride, which remained elastic and " tacky " after 20 hours' heating.

Pyrolysis at higher temperatures caused considerable loss in weight (25% at 500°; 44% at 600°), large quantities of ethylene were formed, and the yield of ethyl acrylate fell to about 40%. The amount of ethyl α-acetoxypropionate recovered was 31% at 500° and 10% at 600°. In all three pyrolyses, acetaldehyde was formed, and identified by its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 156—159°; the amount was small at 450°, but much larger at 500° and 600°.

A fourth pyrolysis was carried out, at 450°, in which silica gel was substituted for half the packing in the tube. There was a 53% loss of weight; the recovered ethyl α-acetoxypropionate amounted to only 13% of the total, and the yield of ethyl acrylate fell to 36%. The silica gel was thickly coated with glistening graphite, but the quartz chips were practically unaltered.

n-Butyl α-Acetoxypropionate.—Preparation. *n*-Butyl lactate (b. p. 86—87°/10 mm.) (438 g.) was gradually added to a mixture of 330 g. (8% excess) of acetic anhydride and 1 c.c. of concentrated sulphuric acid kept at 40—45°. After standing over-night, the whole was fractionated; 520 g. of almost pure *n*-butyl α-acetoxypropionate were obtained (92% yield), and 29 g. (8% yield) of *n*-butyl acetate. *n-Butyl α-acetoxypropionate* is a colourless mobile liquid, with a pleasant fruity odour. It is soluble in acetone, alcohol, and ether, and boils at 105°/15 mm., 111°/19 mm., 126°/41 mm., and 213—214°/767 mm. It has $n_D^{24°}$ 1·4147 and $d_4^{20°}$ 1·0001 (Found : C, 57·3; H, 8·5. $C_9H_{16}O_4$ requires C, 57·4; H, 8·5%).

A preliminary preparation, in which the reaction mixture was kept for a week, and heated (intermittently) at 100° for 50 hours, gave only a 27% yield of the desired ester, but a 61% yield of *n*-butyl acetate.

Pyrolysis. The pure ester was run at the rate of 4·5 g./min. into the pyrolysis tube. At 450—460°, 61% was recovered unchanged; at 510—530°, 46%; and at 560—580°, 11%.

260 G., pyrolysed at 510—530°, yielded 208·5 g. of liquid, which on distillation gave (i) 5 g., b. p. < 100°, (ii) 57 g., b. p. 100—175°, (iii) 27 g., b. p. 190—208°, (iv) 90 g., b. p. 208—213°, and (v) 5 g. of residue. The loss in weight was probably due to acetaldehyde, which was identified in fraction (i) as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 157—159°. Fraction (ii) consisted mainly of acetic acid and *n*-butyl acrylate : the latter was obtained in a slightly crude form (27 g.) by extracting the fraction with brine, but though carefully refractionated, it could not be rigorously purified. Fractions (iii), (iv), and (v) were mainly unchanged *n*-butyl α-acetoxypropionate.

n-Butyl acrylate is a colourless mobile liquid, with the characteristic fresh pleasant odour of the acrylates. Heated at 100° with 1% of benzoyl peroxide for some hours, it polymerises to a soft, plastic, almost colourless polymeride, which does not harden on prolonged heating. The monomeride boils at 59°/23 mm. and has $n_D^{17·5°}$ 1·420 and $d_{20°}^{20°}$ 0·906 (Found : C, 64·6; H, 9·3. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%).

The exit gases from the pyrolysis tube were passed through two wash-bottles containing bromine, from which crude αβ-dibromobutane was obtained. On refractionation, this had b. p. 166—167°, but was still slightly impure (Found : Br, 73·4. Calc. : Br, 74·1%). The exit gases from the wash-bottles consisted of carbon monoxide, residual ethylene, and the carbon dioxide which was passed slowly through the tube during the pyrolysis.

The yields of crude *n*-butyl acrylate were 15% at 450—460°, 24% at 510—530°, and 18% at 560—580°.

Benzyl α-Acetoxypropionate.—Preparation. Ethyl lactate and benzyl alcohol in equimolecular proportion were heated during 20 hours from 150° to 200°, about 90% of the theoretical amount of ethyl alcohol being eliminated; the residue was fractionated. The benzyl lactate, b. p. 134°/4 mm., $n_D^{23·5°}$ 1·5049, $d_4^{20°}$ 1·1355 (yield, 75%), and a slight excess of acetic anhydride (trace of sulphuric acid) below 70° gave after a few days a 70% yield of *benzyl α-acetoxypropionate*, b. p. 145—148°/4 mm., $n_D^{21°}$ 1·4874, $d_4^{20°}$ 1·1227 (Found : C, 63·5; H, 6·3. $C_{12}H_{14}O_4$ requires C, 64·8; H, 6·3%).

Pyrolysis. 100 G. of the ester were run at the rate of 3 g./min. into the pyrolysis tube at 530°. 84 G. of liquid were collected, which on fractionation yielded 52 g., b. p. 120°/75 mm.— 150°/15 mm., and 18·5 g. of recovered acetoxy-ester, b. p. 150°/5 mm. The former fraction was washed with brine, and aqueous potassium carbonate, until free from acetic acid, yielding 42 g. of crude benzyl acrylate (74% yield). Two further fractionations gave 14 g. of pure *benzyl acrylate*, a pleasant-smelling, colourless, mobile liquid, b. p. 94°/6 mm., 213°/760 mm., $n_D^{20°}$ 1·5143, $d_4^{20°}$ 1·0573 (Found : C, 74·0; H, 6·3. $C_{10}H_{10}O_2$ requires C, 74·1; H, 6·2%).

Methyl α-Carbethoxyethyl Phthalate.—*Preparation.* Ethyl lactate and methyl hydrogen phthalate in equimolecular proportion were refluxed with an equal volume of benzene, containing 0·5% by weight of concentrated sulphuric acid. The water formed was progressively removed from its azeotropic mixture with the benzene, and the residue distilled in a vacuum, giving *methyl α-carbethoxyethyl phthalate* as a colourless oil, b. p. 140°/3 mm., $n_D^{20°}$ 1·4970, $d_4^{20°}$ 1·1632 (Found : C, 59·9; H, 5·8. $C_{14}H_{16}O_6$ requires C, 60·0; H, 5·7%).

Pyrolysis. 140 G. of the ester were run into the pyrolysis tube, at 550°, at the rate of 2·5 c.c./min. The condensed product (99 g.) was a pasty semi-solid mass; on filtration and washing with small amounts of ether, 35 g. of phthalic anhydride were obtained. The filtrate was fractionated : acetaldehyde was detected in the first (ethereal) fraction, and characterised as its 2 : 4-dinitrophenylhydrazone; 25 g. of liquid were then collected, b. p. 50—140°, followed by 25 g. of the unchanged phthalate. The fraction of b. p. 50—140°, on further fractionation, yielded 5 g. of methyl alcohol (characterised as its 3 : 5-dinitrobenzoate) and 18 g. of crude ethyl acrylate, b. p. 101—105° (yield, 41%). This readily polymerised in the usual way, in presence of 0·5% of benzoyl peroxide.

α-Acetoxypropionitrile (*α-Cyanoethyl Acetate*).—*Preparation.* Redistilled acetaldehyde cyanohydrin, heated with acetic anhydride (1 mol.)–sulphuric acid for ¼ hour at 100°, gave pure α-acetoxypropionitrile, b. p. 80—82°/25 mm., $n_D^{20°}$ 1·403, in 90% yield. When heating was carried out for 18 hours (including 5 hours at 170°) in presence of a little perchloric acid, the yield of α-acetoxypropionitrile fell to 40% and a high-boiling fraction was obtained, which yielded slightly impure *N*-acetyl-α-acetoxypropionamide, m. p. 65—70° (from ethyl alcohol) (Found : C, 48·2; H, 6·4; N, 9·4 to 10; *M*, cryoscopic in benzene, 171. Calc. for $C_7H_{11}O_4N$: C, 48·6; H, 6·4; N, 8·1%; *M*, 173). Colson (*Bull. Soc. chim.*, 1897, **17**, 55) records m. p. 75°.

When acetaldehyde cyanohydrin was refluxed with excess of glacial acetic acid, along with benzene to bring about azeotropic removal of any water formed, acetylation proceeded to the extent of almost 70% in 48 hours, but could not be carried further.

Pyrolysis. 113 G. of pure α-acetoxypropionitrile were run at the rate of 4·5 g./min. into the pyrolysis tube at 540—550°. 108 G. of liquid were collected, which yielded 72 g. of recovered α-acetoxypropionitrile (64% of total) and 18 g. of slightly crude acrylonitrile (95% yield). This on fractionation yielded acrylonitrile, b. p. 76—78°/759 mm. (Found : C, 67·7; H, 5·7. Calc. for C_3H_3N : C, 67·9; H, 5·7%). In addition, acetaldehyde and hydrogen cyanide were detected in the pyrolysis product, the former as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 152—156°, the latter as its silver salt. These two substances were also obtained in the pyrolysis at 440—460°.

β-Acetoxypropionitrile (*β-Cyanoethyl Acetate*).—*Preparation.* The nitrile was prepared in 78% yield from ethylene cyanohydrin and acetic anhydride in presence of a little concentrated sulphuric acid. It had b. p. 210—212°/773 mm. Henry (*Compt. rend.*, 1886, **102**, 771) records b. p. 205—208°.

Pyrolysis. This was carried out at three temperatures, as summarised in the table on p. 403. The three products were united and fractionated : the first fraction was washed with brine till free from acetic acid, and gave a 63% yield of crude acrylonitrile (calculated as usual on the acetoxy-nitrile destroyed). This was dried over calcium chloride, then over phosphoric oxide, and fractionated, yielding acrylonitrile, b. p. 76—78°/761 mm. (Found : C, 67·4; H, 5·7%).

Pyrolysis of Ethyl Acetate.—Purified commercial ethyl acetate, b. p. 78—79°/760 mm., was pyrolysed at three different temperatures (see table). In each case, the degree of pyrolysis was determined by titration after an aliquot portion of the resulting mixture of acetic acid and unchanged ester had been boiled with a known excess of alkali.

Pyrolysis of cycloHexyl Acetate.—Purified commercial *cyclo*hexyl acetate, b. p. 175·5—176°/750 mm., was pyrolysed at three different temperatures, with results summarised in the table. In each case, on distillation of the crude product, the first fraction (b. p. < 90°) separated into two layers, of which the bottom layer, a few c.c., was strongly acid. This separation was due to water produced by pyrolysis of a trace of *cyclo*hexanol present in the ester : for it was found

that, although *cyclo*hexene and glacial acetic acid are completely miscible, addition of a mere trace of water causes separation into two layers.

The *cyclo*hexene was separated by washing the first fractions (hydrocarbon plus acetic acid) with brine. The *cyclo*hexene produced at 550° was given a final wash with aqueous potassium carbonate, and carefully dried ($d_4^{20°}$ 0·8211; iodine value 254). It was then fractionated: a portion, b. p. 80—83°, was rejected, and a fraction, b. p. 83—84°/761 mm., collected, having $d_4^{20°}$ 0·8117 (Found: C, 87·5; H, 12·1; iodine value, 286. Calc. for C_6H_{10}: C, 87·8; H, 12·2%; iodine value, 310. Calc. for C_6H_6: C, 92·3; H, 7·7%; iodine value, 0). It seems likely that the crude *cyclo*hexene was originally contaminated by a little benzene, produced at 550° by pyrolytic dehydrogenation, this being largely eliminated on further fractionation.

1-*Cyano*cyclo*hexyl Acetate.—Preparation.* *cyclo*Hexanone cyanohydrin was prepared by running 193 c.c. of hydrogen cyanide into 480 g. of commercial *cyclo*hexanone in the presence of a little aqueous caustic potash, the temperature being maintained at 40—50°. After 30 minutes' stirring, 7·5 c.c. of concentrated sulphuric acid were added, slowly followed by 550 g. of acetic anhydride. The product was distilled in a vacuum: the fraction having b. p. 80—130°/5 mm. was refractionated, yielding 375 g. of pure 1-*cyano*cyclo*hexyl acetate*, b. p. 110—115°/5 mm. (nearly all at 112—113°/5 mm.). The product remained liquid unless shaken, or strongly cooled; it then rapidly and completely crystallised: the refractive index of the supercooled liquid was readily obtainable. The acetate crystallised well from ligroin, in fine matted fibrous needles, m. p. 48—49°, b. p. 112—113°/5 mm., $n_D^{20°}$ 1·4585 in the liquid state (Found: C, 65·0; H, 7·7; N, 8·8; *M*, cryoscopic in benzene, 167. $C_9H_{13}O_2N$ requires C, 64·7; H, 7·8; N, 8·4%; *M*, 167).

Pyrolysis. This was carried out at three different temperatures (see table). The solid ester was melted, and heated to 80° before being placed in the dropping-funnel, in order to prevent crystallisation.

The crude product of pyrolysis at 440—450° was distilled in a vacuum to remove the acetic acid and 1-cyano*cyclo*hexene from the unchanged acetoxy-compound. The first few grams smelt strongly of hydrogen cyanide and gave a curdy precipitate on addition of silver nitrate. On redistillation of these low-boiling fractions, a few drops were collected at about 140°, which yielded a 2 : 4-dinitrophenylhydrazone, m. p. 152—155°, alone or mixed with authentic *cyclo*hexanone-2 : 4-dinitrophenylhydrazone. The 1-cyano*cyclo*hexene was washed with brine till free from acetic acid, then with aqueous potassium carbonate, dried, and fractionated. A pure sample, b. p. 78—80°/12 mm., was obtained (Found: C, 78·2; H, 8·4. Calc. for C_7H_9N: C, 78·5; H, 8·4%). Van Coillie records b. p. 73·9—74·2°/11·5 mm. (*Bull. Soc. chim. Belg.*, 1933, **42**, 419).

The authors wish to thank the Directors of Imperial Chemical Industries Limited for permission to publish this work.

OBITUARY NOTICES.

JOHN DENTON.

1882—1934.

JOHN DENTON was born at Great Horton and died in his 53rd year at Denholme, near Bradford, on June 18th, 1934. He leaves a widow.

Denton was a student at the Bradford Technical College, and in 1903 began his industrial career as a chemist at the Crossley Hall Dyeworks of William North & Co., Ltd. His work soon led to several improvements of commercial importance and he attained an influential position whilst comparatively young. He also occupied the position of manager of the Silsden Dyeing Co., Ltd., from 1912 to 1914, and in 1919 at Keighley he became a member of the firm of Denton Bros., dyers and bleachers.

In later years he was interested in designing electrical recording instruments. For example, with a Keighley friend, he invented the " electrograph." This was not merely a speedometer, but was designed to chart also stops and their duration, and in the event of accident, registered the time of the mishap and the speed at which the car was then travelling.

Denton became a Fellow of the Chemical Society in 1906 and an Associate of the Institute of Chemistry in 1920; but he was most actively concerned with the Society of Dyers and Colourists, which he joined in 1898, subsequently serving as a member of the Publication Committee and Council, Hon. Treasurer, and Vice-President, successively, of this Society.

He served during the War with the 3rd/2nd West Riding Brigade, R.F.A.; he went to France with the 49th Division and was badly gassed; although he went to the front again, his health compelled his return to this country and he retired with the rank of Captain. He was an active supporter of the British Legion.

Denton was enthusiastic in all causes into which he entered and his enthusiasm was contagious. Full of energy, straightforward in character and speech, he was generous to a fault. He had a great love of horses and probably was never happier than when in the saddle. He was a familiar figure at agricultural shows in the North and often acted as judge in equestrian jumping classes.

F. M. ROWE.

GEORGE WILLIAM FRASER HOLROYD.

1871—1934.

THE only son of Colonel W. G. M. Holroyd of the Bengal Staff Corps, who was afterwards Director of Public Instruction in the Punjab, G. W. F. Holroyd was for a short time at Winchester, but on account of delicate health was educated privately and went to Christ Church, Oxford, in 1889 as Fell Exhibitioner. Here he obtained a First in the Final Honours School of Natural Science in 1893 and took the B.A. in 1895. After an interval spent in the analytical laboratory of Fresenius in Wiesbaden he spent two years in research in organic chemistry under Thiele in Munich. At Christ Church—as an undergraduate from 1889 to 1893, as assistant to Vernon Harcourt, 1897—1899, and demonstrator and lecturer, 1899—1903—Holroyd is best remembered by his contemporaries as the first President of the Alembic Club. One of its founders states : " This was a club formed by a number of (then) junior undergraduates because the existing Chemical Club was filled up with seniors. The original members asked Holroyd to be President and I remember him as very enthusiastic and helpful. The first meeting was in the spring of 1901, and in a photograph of the Club taken in 1902 there are 16 members including Holroyd."

After a year spent as Science Master at Bristol Grammar School in 1905 Holroyd went into industry, was employed as chemist to a firm in the heavy chemical industry on the

South Coast, and became very largely occupied in the working up of residuals from the manufacture of coal gas. He was of a slender physique and not of a combative nature, but in August, 1914, he enlisted in the Royal Sussex Regiment and transferred to the Special Gas Section of the Royal Engineers in 1915. Towards the end of 1916, when the demand for chemists with industrial experience became urgent, he was sent home and until the end of the War was occupied in the synthetical production of phenol. The remainder of his life was spent in technical education, and many students of the Blackburn Technical College during the years 1919—1934, where he was Vice-Principal and Head of the Chemistry Department, owe much to his enthusiasm and ability.

Holroyd's work was characterised by meticulous accuracy, and a dogged persistence in overcoming all the details of any problem confronting him. His career as a research student in Munich (1894—1896) was wrecked as far as official recognition was concerned by his persistence in the time-consuming, but self-imposed job of improving the technique for the preparation of liquid hydrogen cyanide and semicarbazide, reagents not readily obtainable in those days. Later (J., 1901, **79**, 1326) he published a detailed description of the electrolytic reduction of nitrourea. This experience probably led him on returning to academic life to the study of the electrolysis of potassium oleate (J., 1924, **125**, 438) and of the electrical conductivity of phosphorus pentachloride (J., 1925, **127**, 2492). Holroyd's scientific friends in later years realised that it was due to a retiring disposition that his output of original work was incommensurate with his critical instinct, deep knowledge, and a laboratory technique persistently improved throughout his whole career.

<div align="right">R. H. PICKARD.</div>

DANIEL J. O'MAHONY.

1860—1934.

DANIEL J. O'MAHONY was born on August 14th, 1860. He received his early education at the Christian Brothers' schools. Intended for the Church, he proceeded to St. Vincent's Seminary and then to St. Sulpice, Paris. He abandoned his clerical studies in 1882. Profiting by his experiences in Paris, he became Superintendent of the Fine Art Department at the Cork Exhibition of 1883.

In 1884 he joined Mr. Denny Lane at the Silverspring starch works, and it was here that his interest in chemistry developed. He became a medical student at Queen's College, Cork, but turned to chemistry, took practical courses in London under Professors Armstrong and Wynter Blyth, and became Demonstrator in Practical Chemistry at the Queen's College under Professors Maxwell Simpson, Senier, and Dixon. Many of the older generation of medical practitioners still pay tribute to the efficiency of his teaching. He became a Fellow of the Chemical Society in June, 1889.

He was appointed Analyst for the Borough of Cork in 1891 ; in 1894 he became analyst for the County of Cork, and, later, for adjoining bodies. He held these posts until his death.

He married in 1900 and had one son and two daughters, who survive him. He was created a Knight of Malta in 1932 on the revival of the Order in the Irish Free State.

In the varied nature of his professional practice he brought to bear a strong element of common sense. He was always ready to advise, but would not fail, when necessary, to point out the limits of his own experience. He had an old-world charm of manner and courtesy, a good sense of humour, and a reputation as a raconteur. Old Cork, its people, things and associations were his particular delight.

In 1928 his health broke down and he had to retire from active participation in the work of the Laboratory. His wife died in 1930. He bore his own long illness with great patience, and passed peacefully away on December 1st, 1934.

<div align="right">D. O'SULLIVAN.</div>

LEWIS GORDON PAUL.
1858—1934.

In the death of Lewis Gordon Paul on December 13th, 1934, at the age of seventy-six, the chemical circles of the North have lost a well-known and highly respected figure. A native of Dundee, Paul began his studies at the Royal College of Chemistry, South Kensington, under Sir Edward Frankland. After three years as Frankland's assistant he went abroad and carried out research in organic chemistry in the Laboratory at Tübingen. On his return to England in 1882, Paul joined the staff of Messrs. Read, Holliday & Sons, Huddersfield, and was appointed chemist at their New York works. Subsequently he returned to the Yorkshire works, where he took out several patents, the chief of which was in connection with the manufacture of nitrate of soda.

In 1900, Paul was appointed Public Analyst of Huddersfield and from that time to his death carried on a private practice as a consultant. His early works experience proved invaluable to him in establishing a high reputation as a textile analyst. He was keenly interested in his practice until a few days before his death, and no man had a higher sense of what constituted honourable professional conduct or maintained to a greater degree the dignity of the profession.

In private life he was a charming companion, of ever-cheerful disposition, and possessing a sense of humour which never failed. To the personal regret that all his colleagues felt at his death, is added the knowledge that the profession is much the poorer through his loss.

H. T. LEA.

CHARLES H. RIDSDALE.
1862—1934.

CHARLES H. RIDSDALE was born in 1862, and began his chemical training at a very early age. He entered the laboratory of J. E. Stead at Middlesbrough in 1876, and it is only natural, therefore, that most of his later work should have been connected with iron and steel. He took part in the pioneering experiments of Thomas and Gilchrist, which culminated in the invention of the basic Bessemer process of steel-making, and made possible the production of low-phosphorus steel from phosphoric ores; and his first paper, read conjointly with Stead before the Iron and Steel Institute, was on basic slag, a product of that process. Later he entered the laboratory of the North-Eastern Steel Works, where he rose to be chief chemist and technical adviser, and during his time here he made frequent contributions to the Iron and Steel Institute and to the Newcastle Section of the Society of Chemical Industry on the microscopic examination of steel, heat treatment, and various analytical methods. He retired from the North-Eastern Steel Co. in 1917, to take up private practice in Middlesbrough as analyst and consulting chemist, where he was later joined by his son, Mr. Noel D. Ridsdale, with whom he continued to work until his death, and who now carries on the practice.

Ridsdale, himself a careful and accurate analyst, was always dissatisfied at discrepancies occurring in the work of different analysts on what professed to be the same sample, and early saw that it would be a valuable help to have samples of commercial substances of authoritatively ascertained composition, on which analysts could check their methods and their practice; and with great perseverance and in face of great difficulties he instituted and developed " British Chemical Standards," a co-operative association of chemists all over the world, who have now issued a large number of standard substances (chiefly, as yet, connected with the metallurgical industries), the uniformity of which has been ascertained by the concordant results of many independent analysts. He has in this way done a real service to the chemical world.

Ridsdale was a Fellow of the Institute of Chemistry, a member of the Iron and Steel Institute, and a member and Past President of the Cleveland Institution of Engineers. He was very careful and accurate, slow and deliberate in his utterances, always thinking before he spoke; respected and liked by all who knew him, upright and trustworthy, a good man to have as a friend. J. T. DUNN.

E E

ERNEST HENRY SANITER.

1863—1934.

ERNEST HENRY SANITER, chief consulting metallurgical chemist to the United Steel Companies, Ltd., was one of the best known metallurgists in the steel trade. Many honours came to him, and in 1910 he was awarded the Bessemer Medal, one of the most highly prized distinctions in the steel world.

Born at Middlesbrough in 1863, Saniter received his early education at Sir William Turner's Grammar School, Coatham, Redcar. For three years he studied chemistry in the metallurgical laboratory of Mr. J. E. Stead, and from 1883 to 1890 was assistant chemist at the North-Eastern Steel Works, Middlesbrough. From 1890 to 1897 he held the position of head chemist at the Wigan Coal and Iron Company, Wigan. During 1891 and 1892 he invented and brought to a successful issue his well-known Saniter process for desulphurising iron and steel.

Early in 1898 Saniter went to Port Clarence, and on behalf of Messrs. Dorman, Long and Co., and Bell Brothers, demonstrated the suitability of common Cleveland iron for making high-class basic open-hearth steel. The success of these experiments resulted in the erection of a 200-ton mixer, eight 50-ton basic open-hearth furnaces, and a rolling mill. In 1904, he resigned his position at Port Clarence in order to take up an appointment with Messrs. Steel, Peech, and Tozer of Sheffield.

His published works include papers on his desulphurising process, on allotropic carbon and iron, on the estimation of manganese in metals and minerals, and on the estimation of chromium in chrome ore and ferrochrome.

He died on November 2nd, 1934, having lived to the age of 71. He was elected a Fellow of the Chemical Society on December 4th, 1890.

B. W. METHLEY.

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89. *The Stereochemical Relationships of Some Optically Active Amines and Amino-acids. Part I. The Configuration of Valine.*

By FRED BARROW and GEORGE W. FERGUSON.

THE method introduced by Clough (J., 1918, **113**, 526 : for further references, see Freudenberg, " Stereochemie," 1932, p. 693) of correlating the stereochemical configurations of similarly constituted, optically active compounds from observations on the alterations in their rotatory power, accompanying the introduction of similar substituents, has been employed by Karrer and van der S. Veer (*Helv. Chim. Acta*, 1932, **15**, 746) to determine the configuration of valine. The naturally occurring, dextrorotatory amino-acid and its ethyl ester, on conversion into the benzoyl, benzenesulphonyl, and other acyl derivatives, showed optical displacements of a similar sign and magnitude to those which accompany the introduction of the same substituents into (+)-alanine (Karrer, Escher, and Widmer, *Helv. Chim. Acta*, 1926, **9**, 301; Freudenberg and Rhino, *Ber.*, 1924, **57**, 1547), and the conclusion was therefore drawn that both acids belong to the same steric series. Since, in the opinion of the present authors, the results obtained by the method of optical displacements are not so trustworthy as those furnished by purely chemical methods, the present investigation was undertaken with the object of determining the relative configurations of valine and alanine by means of chemical transformations.
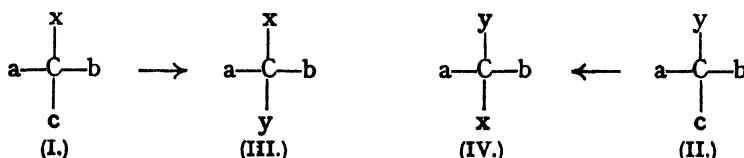

The method employed depends on the following principle : if two optically active compounds, Cabcx and Cabcy, having the same stereochemical configurations (I) and (II),

are each converted into Cabxy by transformation of a common group c into y and x respectively, the two compounds (III) and (IV) produced will have opposite configurations, provided that the reactions used in effecting the transformations do not involve, at any stage, a Walden inversion owing to the rupture of the group c from the asymmetric atom.

In order to apply this principle to the determination of the relative configurations of valine and alanine, it is necessary to convert the carboxyl group in the first-named acid into the methyl group, and the carboxyl of alanine must be transformed into the *iso*propyl group. If the two α-methyl*iso*butylamines (IX) and (XIV) produced have opposite signs of rotation, the original amino-acids (V) and (X) must have the same stereochemical configuration.

The reactions employed to effect the transformations are shown in the scheme :
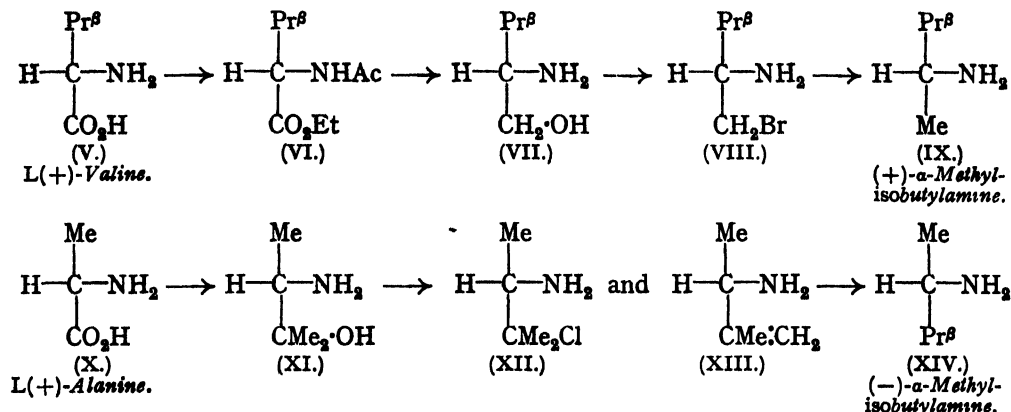
The α-methyl*iso*butylamine obtained from (+)-alanine gave a lævorotatory hydrochloride, and that from (+)-valine furnished a dextrorotatory hydrochloride : the *p*-nitrobenzoyl derivatives of the two amines also showed opposite signs of rotation. From these results it is definitely established that the naturally occurring, dextrorotatory valine has the same stereochemical configuration as (+)-alanine. Roger's modification (*Helv. Chim. Acta*, 1929, **12**, 1060) of Freudenberg's method of denoting both the configuration and the sign of rotation being adopted, the amino-acid will be designated $L(+)$-valine.

*Conversion of $L(+)$-Valine into (+)-α-Methyl*iso*butylamine.*—The formyl derivative of $L(+)$-valine (V), when boiled with alcoholic hydrogen chloride, underwent simultaneous hydrolysis and esterification, yielding valine ester hydrochloride, which, on acetylation, gave *ethyl $L(-)$-α-acetamido*iso*valerate* (VI), $[\alpha]_{5461} - 20·1°$. The acetylation was accompanied by slight racemisation, since the valine hydrochloride obtained from the ester by hydrolysis had a rotatory power, $[\alpha]_D + 27·1°$, somewhat lower than that of the optically pure hydrochloride, $[\alpha]_D + 28·8°$. On reduction with sodium and alcohol, the acetyl ester yielded $L(+)$-*valinol* (VII), the main portion of which (A), after isolation in the form of its *hydrochloride*, had $[\alpha]_{5461} + 1·2°$. Since the optically pure hydrochloride obtained by the resolution of inactive valinol had $[\alpha]_{5461} + 16·4°$, the reduction of the ester was accompanied by profound racemisation. In view of this small rotation and also of the fact that we propose to utilise the active valinols as reference compounds for correlating the configuration of other amino-acids, it became necessary to establish beyond doubt that the optical activity of the reduction product was actually due to the amino-alcohol and not to some impurity, whose presence would not be revealed by analysis; and this was ultimately accomplished by a comparison of its benzoyl derivatives with those of the fully active valinol.

The resolution of inactive valinol was readily effected by crystallisation of its hydrogen (+)-tartrate from alcohol, and the hydrochlorides of both the $D(-)$- and the $L(+)$-amino-alcohol were obtained in a pure condition. On benzoylation in the presence of aqueous sodium hydroxide, $L(+)$-valinol gave a lævorotatory ON-*dibenzoyl* derivative (XV),

$[\alpha]_{5461} - 20\cdot1°$, which was converted, by heating with an excess of benzoyl chloride in the presence of pyridine, into a dextrorotatory *tribenzoyl* derivative (XVI), $[\alpha]_{5461} + 133\cdot1°$.

(XV.)   Pr$^\beta$·CH·NHBz   Pr$^\beta$·CH·NBz$_2$ (XVI.)
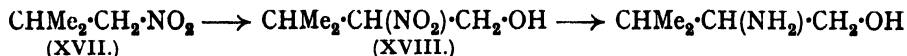   CH$_2$·OBz   CH$_2$·OBz
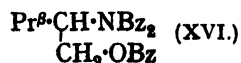
The successive conversion of $L(+)$-valinol into its di- and tri-benzoyl derivatives is, in each case, accompanied by a reversal in the sign of the rotation. A similar behaviour was shown by the feebly active valinol, obtained by the reduction of $L(-)$-acetamidoisovalerate, the dibenzoyl derivative being lævorotatory, $[\alpha]_{5461} - 1\cdot3°$, and the tribenzoyl derivative dextrorotatory, $[\alpha]_{5461} + 3\cdot3°$. From these results there can be no doubt that the activity shown by the reduction product of the ester is due to the presence of $L(+)$-valinol hydrochloride. Further confirmation was furnished later by the isolation, from the mother-liquors from which the feebly active hydrochloride had been removed, of a very small amount of $L(+)$-valinol hydrochloride (B) having a rotatory power, $[\alpha]_{5461} + 14\cdot5°$, almost equal to that of the fully active compound, and showing the same alternation in the sign of the rotation on conversion into its di- and tri-benzoyl derivatives. The comparison of the rotations of these derivatives is facilitated by the table given below, in which the values for the specific rotations (for λ 5461) have been collected :

Derivative.	*l.*-Valinol from resolution.	*L*-Valinol from reduction.	
		A.	B.
Hydrochloride	$+ 16\cdot4°$	$+ 1\cdot2°$	$+ 14\cdot5°$
Dibenzoyl	$- 20\cdot1$	$- 1\cdot3$	$- 18\cdot1$
Tribenzoyl	$+ 133\cdot1$	$+ 3\cdot3$	$+ 117\cdot0$

The reduction of $L(+)$-valinol (VII) to α-methyl*iso*butylamine (IX) was accomplished by heating the hydrochloride with hydrogen bromide in acetic acid solution, and reducing the resulting α-*bromomethylisobutylamine hydrobromide* (as VIII) catalytically in the presence of palladised charcoal. The (+)-α-*methylisobutylamine hydrochloride* obtained had only a small rotation, $[\alpha]_{5461} + 3\cdot5°$, but gave a strongly active *p*-nitrobenzoyl derivative, $[\alpha]_{5461} - 55\cdot8°$.

$D(-)$-Valinol was reduced in a similar manner, and the resulting (−)-α-*methylisobutylamine* furnished a *hydrochloride*, having $[\alpha]_{5461} - 3\cdot4°$, and a p-*nitrobenzoyl* derivative with $[\alpha]_{5461} + 55\cdot8°$. In view of this identity in the magnitude of the rotations of the two isomerides, it would appear that the reduction of the active valinols is not attended with any racemisation.

The inactive valinol required for the resolution was prepared partly from inactive valine by conversion into ethyl α-acetamido*iso*valerate, followed by reduction with sodium and butyl alcohol, and partly by the method illustrated in the following scheme :

CHMe$_2$·CH$_2$·NO$_2$ $\longrightarrow$ CHMe$_2$·CH(NO$_2$)·CH$_2$·OH $\longrightarrow$ CHMe$_2$·CH(NH$_2$)·CH$_2$·OH
(XVII.)   (XVIII.)

α-Nitro*iso*butane (XVII), prepared from *iso*butyl iodide and silver nitrite, was condensed with formaldehyde by Shaw's method (*Rec. trav. chim.*, 1898, **17**, 50), and the resulting β-*nitroisoamyl alcohol* (XVIII) reduced with iron and hydrochloric acid. Although the reduction of the nitro-alcohol to valinol proceeded very smoothly, this method of preparation possessed no advantages over the alternative method on account of the poor yields in the earlier stages of the synthesis.

Conversion of L(+)-*Alanine into* (−)-α-*Methylisobutylamine.*—$L(+)$-Alanine (X) was esterified, and the ethyl ester hydrochloride treated with methylmagnesium iodide. The (+)-β-*hydroxy-α-methylisobutylamine hydrochloride* (XI) produced had a rotatory power, $[\alpha]_{5461} + 5\cdot6°$, somewhat less than that of the fully active amino-alcohol, $[\alpha]_{5461} + 6\cdot1°$, prepared by the resolution of the inactive compound, but gave a N-*benzoyl* derivative having the full activity. The resolution of the inactive alcohol was effected by the crystallisation of the *hydrogen* (+)-*tartrate* from alcohol, the *hydrochloride* of the (+)-*amino-alcohol* being readily isolated in a pure condition. The *hydrochloride* of (−)-β-*hydroxy-α-methylisobutylamine* could not be obtained entirely free from the stereoisomeric form,

but the N-*benzoyl* derivative was prepared in an optically pure condition by crystallisation from light petroleum. The reduction of (+)-β-hydroxy-α-methyl*iso*butylamine (XI) to (—)-α-methyl*iso*butylamine (XIV) at first presented some difficulty. The method, successfully employed in the case of the valinols, failed when applied to the isomeric amino-alcohol. Heating with hydrobromic acid under various conditions caused profound decomposition, the greater part of the nitrogen being eliminated in the form of ammonia, and the small amount of α-methyl*iso*butylamine, isolated from the product after catalytic reduction, was completely inactive. The conversion of the (+)-amino-alcohol into (—)-α-methyl*iso*-butylamine was ultimately accomplished by treatment of the hydrochloride with phosphorus pentachloride in chloroform solution, followed by catalytic reduction in the presence of palladised charcoal. The action of phosphorus pentachloride results in the formation of a mixture of the *chloro-amine* (XII) and the unsaturated *amine* (XIII), both of which readily undergo reduction. Some racemisation takes place during the interaction with phosphorus pentachloride, for the rotatory power of the (—)-*α-methylisobutylamine hydrochloride* varied in different experiments from $[\alpha]_{5461}$ — 1·35° to — 2·65°, and was always lower than that of the corresponding hydrochloride (± 3·5°) obtained by the reduction of the active valinols. The rotation of the p-*nitrobenzoyl* derivative varied from $[\alpha]_{5461}$ + 44·1° to + 47·4°, but could be raised by repeated crystallisation to a value (+ 53·8°) almost equal to that of the fully active compound.

In view of the fact that the optically active forms of benzoylalanine may be readily obtained by the method of resolution described by Pope and Gibson (*J.*, 1912, **101**, 939), experiments were undertaken, during the earlier part of this investigation, in the hope of utilising the benzoyl derivatives in place of the free amino-acids for effecting similar transformations to those described above. It was found that inactive benzoylalanine could be smoothly converted, by direct esterification at the ordinary temperature, into its methyl ester, which furnished the N-benzoyl derivative of β-hydroxy-α-methyl*iso*butylamine in excellent yield, when treated with methylmagnesium iodide. Attempts to reduce this benzoyl derivative under various conditions were unsuccessful. Moreover, the benzoyl derivative could not be hydrolysed without undergoing extensive decomposition, and further experiments in this direction were therefore abandoned.

EXPERIMENTAL.

All temperatures are corrected.

Preparation of Inactive Valinol.—This amino-alcohol has been prepared by Karrer, Gisler, Horlacher, Locher, Mäder, and Thomann (*Helv. Chim. Acta*, 1922, **5**, 478) from valine ethyl ester by reduction with sodium and ethyl alcohol. A much better yield is obtained by reducing the acetyl derivative of the ester in butyl-alcoholic solution and isolating the amino-alcohol by steam distillation. The acetyl ester was more conveniently prepared by the following procedure than by that of Karrer, Miyamichi, Storm, and Widmer (*ibid.*, 1925, **8**, 205).

Valine (50 g.) was esterified with alcohol (300 c.c.) and hydrogen chloride in the usual manner and, after removal of the excess of alcohol under reduced pressure, the residual valine ester hydrochloride was heated for 1 hour on the steam-bath with anhydrous sodium acetate (50 g.) and acetic anhydride (200 g.). The acetic anhydride was distilled under diminished pressure, and the residue extracted with chloroform : distillation of the chloroform extract gave ethyl α-acetamido*iso*valerate as a viscid oil (59 g.), b. p. 157—158°/21 mm., having a faint garlic odour (Found : N, 7·8. Calc. : N, 7·5%).

The reduction to valinol was effected by rapidly adding sodium (19 g.) to a boiling solution of the ester (12 g.) in butyl alcohol (160 c.c.), which had been dehydrated by distillation over magnesium butyloxide (Lund and Bjerrum, *Ber.*, 1931, **64**, 210). After 1 hour's boiling, water was added, and the mixture distilled in steam until the distillate was no longer alkaline. Valinol is only slowly volatile in steam and the vapours have a pronounced odour resembling that of crude acetamide. The distillate was acidified with hydrochloric acid, the aqueous layer separated and evaporated, the residue warmed with butyl alcohol, and the solution filtered from a small amount of ammonium chloride. On the addition of ether to the butyl-alcoholic solution, valinol hydrochloride separated ; it crystallised from acetone in small, lustrous, hygroscopic plates (4 g.), m. p. 118—119° (Karrer *et al.*, *loc. cit.*, give 114°) (Found : N, 10·0; Cl, 25·6. Calc. : N, 10·0; Cl, 25·4%).

Valinol was also prepared as follows : α-nitro*iso*butane was condensed with formaldehyde as described by Shaw (*loc. cit.*), and the resulting β-nitro*iso*amyl alcohol (14 g., b. p. 98°/7 mm.) reduced by heating on the steam-bath with iron powder (17 g.) and alcohol (100 c.c.) whilst hydrochloric acid (90 c.c. of 5N) was gradually added. After 12 hours the alcohol was removed by distillation, and the valinol liberated by the addition of sodium hydroxide, distilled in steam, and isolated as its hydrochloride in the manner described previously (yield, 90%) (Found : N, 10·0%).

The N-*monobenzoyl* derivative of valinol was prepared by shaking a solution of the hydrochloride (1 g.) and potassium carbonate (5 g.) in water (20 c.c.) with benzoyl chloride (1·2 g.) dissolved in ether (5 c.c.). The dried ethereal extract gave a gummy residue, which crystallised from light petroleum in colourless needles (0·6 g.), m. p. 81—82° (Found : N, 6·6. $C_{12}H_{17}O_2N$ requires N, 6·8%). The *dibenzoyl* derivative, prepared in a similar manner with an excess of benzoyl chloride (3 mols.) and aqueous sodium hydroxide, separated from aqueous methyl alcohol in long stout prisms, m. p. 114° [Found : C, 73·2; H, 6·9; N, 4·6; *M* (Rast), 334. $C_{19}H_{21}O_3N$ requires C, 73·2; H, 6·8; N, 4·5%; *M*, 311]. *Tribenzoyl* derivative : benzoyl chloride (1 c.c.) was gradually added to dibenzoylvalinol (0·15 g.) dissolved in pyridine (5 c.c.), and the mixture heated for 1 hour on the steam-bath. After 24 hours at room temperature, the mixture was boiled with water; the resulting brown resin crystallised from aqueous alcohol in small lustrous plates (0·15 g.), m. p. 135° [Found : C, 75·3; H, 6·0; N, 3·6; *M* (Rast), 428. $C_{26}H_{25}O_4N$ requires C, 75·2; H, 6·1; N, 3·4%; *M*, 415].

Reduction of Inactive Valinol to α-Methylisobutylamine.—A solution of valinol hydrochloride (3 g.) in glacial acetic acid (12 c.c.) was saturated with hydrogen bromide at − 15° and heated in a sealed tube for 10 hours at 130—140°. The solid obtained by evaporation under reduced pressure was dissolved in alcohol, and the solution filtered from ammonium bromide. On the addition of ether, α-*bromomethylisobutylamine hydrobromide* (2·7 g.) separated. It still contained a little ammonium bromide, from which it was freed by solution in warm butyl alcohol and re-precipitation with ether; slender lustrous needles, m. p. 211—212° (decomp.) with previous darkening at 203° (Found : Br, 64·4. $C_5H_{13}NBr_2$ requires Br, 64·7%).

The catalytic reduction of the preceding bromo-compound was carried out by shaking the hydrobromide (1 g.), dissolved in aqueous acetic acid (30 c.c. of 7·5%) containing sodium acetate (1 g.), with palladised charcoal (4 g. containing 10% of the metal) in hydrogen at room temperature and pressure. Reduction was complete in 80 minutes, almost the theoretical amount of hydrogen being absorbed (reduction proceeded very slowly and was incomplete if the sodium acetate was omitted). After filtration from the catalyst, the solution was made alkaline with sodium hydroxide and distilled. Neutralisation of the distillate with hydrochloric acid, followed by evaporation, gave a solid, which crystallised from acetone, a small amount of ammonium chloride being removed by filtration ; α-methyl*iso*butylamine hydrochloride separated in long lustrous needles (0·4 g.), m. p. 203° (Found : Cl, 28·8. Calc. : Cl, 28·7%). The p-*nitro-benzoyl* derivative was prepared by shaking a solution of the hydrochloride (0·25 g.) and sodium carbonate (0·45 g.) in water (10 c.c.) for 20 minutes with *p*-nitrobenzoyl chloride (0·45 g.) dissolved in benzene (10 c.c.). The residue from the dried benzene extract crystallised from *cyclo*hexane in very slender, felted needles (0·42 g.), m. p. 115° (Found : C, 61·1; H, 6·9; N, 11·8. $C_{12}H_{16}O_3N_2$ requires C, 61·0; H, 6·8; N, 11·9%).

For purposes of comparison α-methyl*iso*butylamine was prepared by the reduction of methyl *iso*propyl ketoxime, which was obtained by gradually adding aqueous potassium hydroxide (11·5 g. in 20 c.c.) to a mechanically stirred mixture of methyl *iso*propyl ketone (17 g.) and hydroxylamine hydrochloride (15 g.), dissolved in water (20 c.c.). After 2 hours, the oxime (12·5 g.) was collected in ether, distilled (b. p. 158—160°; compare Nageli, *Ber.*, 1883, **16**, 2984) and reduced in boiling amyl-alcoholic solution (300 c.c.) with sodium (25 g.). The resulting amine was isolated by distillation in steam and converted into its hydrochloride (11·5 g.) (Found : N, 11·2. Calc. : N, 11·3%), which had m. p. (and mixed m. p.) 203°, and gave a *p*-nitrobenzoyl derivative, m. p. (and mixed m. p.) 115°. The hydrochloride has been described by Trasciatti (*Gazzetta*, 1899, **29**, 92), who prepared the amine by reducing α-methyl α-cyano*iso*propyl ketoxime with sodium and alcohol.

Resolution of Valinol.—Freshly precipitated silver oxide (from 25 g. of the nitrate) was shaken with valinol hydrochloride (14·2 g.) dissolved in water (300 c.c.), for 20 minutes. On the addition of (+)-tartaric acid (16 g.) to the filtered solution, a slight precipitate of silver tartrate was produced, which was decomposed by passing hydrogen sulphide through the hot liquid. The gummy residue, obtained after removal of the silver sulphide and evaporation of the solution under diminished pressure, was dissolved in alcohol (100 c.c.) and kept in the ice-chest over-night.

The crop which separated was crystallised from alcohol and consisted of D(—)-*valinol hydrogen* (+)-*tartrate*, long prismatic needles (7·1 g.), m. p. 116°, containing $1H_2O$; it had $[\alpha]_{5461}^{20°} + 10·2°$, $[\alpha]_{5780}^{20°} + 9·5°$ in water ($c = 4·92, l = 2$), this value remaining unchanged on further crystallisation (Found : loss on drying in a vacuum at 100°, 6·7; N, 5·0. $C_9H_{19}O_7N,H_2O$ requires H_2O, 6·6; N, 5·2%). The *hydrochloride*, prepared by addition of aqueous sodium hydroxide to the tartrate, distillation in steam, neutralisation of the distillate with hydrochloric acid, and evaporation, crystallised from acetone in small lustrous plates, m. p. 113°, and gave $[\alpha]_{5461}^{20°} - 16·5°$, $[\alpha]_{5780}^{20°} - 14·7°$ ($l = 2, c = 6·22$) in water (Found : N, 9·9; Cl, 25·4. $C_5H_{13}ON,HCl$ requires N, 10·0; Cl, 25·4%).

The first alcoholic filtrate from the preceding tartrate was diluted with acetone (800 c.c.) and kept at room temperature for 24 hours. After decantation from the gummy solid which separated, the solution was evaporated, and the amino-alcohol isolated from the residual tartrate in the form of its hydrochloride, in the same manner as described for the enantiomorph. The crude product was freed from ammonium chloride by solution in warm butyl alcohol, followed by precipitation with ether, and crystallised from acetone. L(+)-*Valinol hydrochloride* had m. p. 112—114°, $[\alpha]_{5461}^{20°} + 16·4°$, $[\alpha]_{5780}^{20°} + 14·7°$ ($c = 6·32, l = 2$) in water (Found : N, 9·9; Cl, 25·3%).

Benzoyl Derivatives of D(—)- *and* L(+)-*Valinols.*—These were prepared in the same manner as described above for the inactive compounds. The *dibenzoyl* derivative of D(—)-*valinol* crystallised from aqueous alcohol in slender needles, m. p. 117°, and had $[\alpha]_{5461}^{21°} + 20·2°$ ($c = 3·97, l = 1$) in pyridine (Found : C, 73·4; H, 6·7; N, 4·6. $C_{19}H_{21}O_3N$ requires C, 73·3; H, 6·8; N, 4·5%); and the *tribenzoyl* derivative in long needles, m. p. 119°, $[\alpha]_{5461}^{20°} - 133·8°, [\alpha]_{5780} - 119·2°$ ($c = 4·536, l = 1$) in pyridine (Found : C, 75·2; H, 6·0; N, 3·6. $C_{26}H_{25}O_4N$ requires C, 75·2; H, 6·1; N, 3·4%). The *dibenzoyl* derivative of L(+)-*valinol* had m. p. 117° and gave $[\alpha]_{5461}^{20°} - 20·1°$, $[\alpha]_{5780}^{20°} - 17·5°$ ($c = 4·60, l = 1$) in pyridine (Found : N, 4·6%); the *tribenzoyl* derivative had m. p. 119°, and $[\alpha]_{5461}^{19°} + 133·1°$ ($c = 4·629, l = 1$) in pyridine (Found : N, 3·5%).

Conversion of L(+)-*Valine into* L(+)-*Valinol Hydrochloride.*—L(—)-Formylvaline was prepared by the resolution of the inactive compound and had $[\alpha]_{5461}^{20°} - 19·9°$, $[\alpha]_{5780}^{20°} - 17·7°$ ($c = 3·646, l = 4$) in water : Fischer (*Ber.*, 1906, **39**, 2320) gives $[\alpha]_D^{20°} - 16·9°$. The formyl derivative (14·7 g.) was hydrolysed and esterified in one operation by heating with alcohol (300 c.c.) saturated with hydrogen chloride. After 2 hours, the excess of alcohol was distilled under reduced pressure, and the residual ester hydrochloride acetylated by heating on the steam-bath for 1 hour with sodium acetate (40 g.) and acetic anhydride (70 c.c.). *Ethyl* L(—)-α-*acetamidoiso-valerate* was isolated, as described for the inactive isomeride, as a colourless viscid liquid (15 g.), b. p. 158°/21 mm., which crystallised in elongated flat plates when kept for several weeks in the ice-chest (Found : N, 7·5. $C_9H_{17}O_3N$ requires N, 7·5%). It gave in the homogeneous condition $n_D^{18°}$ 1·4517; $d_4^{18°}$ 1·028; $[R_L]_D$ 49·08 (calc., 49·24); $\alpha_{5461}^{18°} - 10·31°$; $\alpha_{5780}^{18°} - 9·15°$; $[\alpha]_{5461}^{18°} - 20·1°$; $[\alpha]_{5780}^{18°} - 17·8°$ ($l = 0·5$). A portion of the ester was hydrolysed by boiling for 2·5 hours with 10 times its weight of hydrobromic acid (12%). The resulting L(+)-valine was isolated in a similar manner to that described by Fischer (*loc. cit.*) for the hydrolysis of the formyl derivative, and gave $[\alpha]_{5461}^{21°} + 32·77°$, $[\alpha]_{5780}^{21°} + 28·56°$ ($l = 2, c = 4·754$) in hydrochloric acid (20%). The value for $[\alpha]_D^{21°} + 27·1°$, calculated from these results, is only slightly lower than that given by Fischer for the optically pure amino-acid, *viz.*, $[\alpha]_D^{20°} + 28·8°$, under the same conditions, and hence the conversion of the L(—)-formyl derivative into L(—)-acetylvaline ethyl ester is not accompanied by any appreciable racemisation.

The reduction of the ester (22 g.) was carried out with sodium (39 g.) and ethyl alcohol (1 l.), dried by distillation from magnesium ethoxide. After being boiled for 30 minutes, the mixture was treated with water, the greater part of the alkali neutralised with hydrochloric acid, and the base steam-distilled and isolated as the hydrochloride in the usual manner. The crude product was decolorised with charcoal in hot butyl alcohol, precipitated by the addition of ether, and crystallised from acetone. The L(+)-*valinol hydrochloride* (3·7 g.) thus obtained had m. p. 116—117°, $[\alpha]_{5461}^{18°} + 1·2°$ ($c = 12·3, l = 2$) in aqueous solution (Found : N, 10·1; Cl, 25·7%); the *dibenzoyl* derivative, m. p. 114—116° (Found : C, 73·6; H, 6·9; N, 4·5%) had $[\alpha]_{5461}^{20°} - 1·3°$ ($c = 7·46, l = 2$) in pyridine, and the *tribenzoyl* derivative, m. p. 136° (Found : C, 75·4; H, 5·8; N, 3·4%), $[\alpha]_{5461}^{21°} + 3·3°$ ($c = 10·4, l = 1$) in the same solvent. The mother-liquors from which the preceding hydrochloride had been separated gave, on evaporation, a pale yellow syrup, which solidified to a brittle resin (0·4 g.) when kept for several weeks in a vacuum over sulphuric acid. This could not be crystallised and contained calcium chloride derived from the charcoal used in decolorising the crude hydrochloride. The volatile base was therefore liberated by steam distillation with aqueous sodium hydroxide and reconverted into the hydro-

chloride. On crystallisation from acetone, a small amount of $L(+)$-valinol hydrochloride (0·13 g.) was obtained having a rotation, $[\alpha]_{5461}^{17\cdot} + 14\cdot5°$ ($c = 2\cdot96$, $l = 1$ in water), only slightly lower than that of the optically pure hydrochloride (m. p. and mixed m. p. 113°. Found: N, 10·2%). It showed the characteristic changes in rotation when converted into its *benzoyl* derivatives; the *dibenzoyl* derivative, m. p. 115—116°, had $[\alpha]_{5461}^{21\cdot} - 18\cdot1°$ ($c = 3\cdot15$, $l = 1$) in pyridine (Found: N, 4·9%), the *tribenzoyl* derivative, m. p. 120°, $[\alpha]_{5461}^{20\cdot} + 117°$ ($c = 1\cdot034$, $l = 1$) in the same solvent (Found: N, 3·6%).

Reduction of the Active Valinols to α-Methylisobutylamine.—$L(+)$-Valinol hydrochloride (0·5 g.) having $[\alpha]_{5461}^{20\cdot} + 16\cdot4°$ was dissolved in glacial acetic acid (10 c.c.) and the solution, after saturation with hydrogen bromide at $- 10°$, was heated in a sealed tube at 100° for 7 hours. The crude α-bromomethylisobutylamine hydrobromide obtained by evaporating the solution under reduced pressure was dissolved in water (40 c.c.) containing sodium acetate (2 g.) and reduced catalytically in the presence of palladised charcoal (2 g. containing 15% of the metal); the theoretical amount of hydrogen was absorbed in 15 minutes. The filtered solution was basified with sodium hydroxide and distilled. Neutralisation of the distillate with hydrochloric acid, followed by evaporation, yielded (+)-*α-methylisobutylamine hydrochloride*, which crystallised from acetone in lustrous slender needles (0·23 g.), m. p. 205° (previous sintering at 192°), $[\alpha]_{5461}^{17\cdot} + 3\cdot5°$ ($c = 6\cdot54$, $l = 1$) in water (Found: N, 11·3; Cl, 28·8. $C_5H_{13}N,HCl$ requires N, 11·3; Cl, 28·7%); the p-*nitrobenzoyl* derivative, prepared as described previously for the inactive isomeride, crystallised from *cyclo*hexane in voluminous, faintly yellow, filamentous needles, m. p. 112°, $[\alpha]_{5461}^{15\cdot} - 55\cdot8°$, $[\alpha]_{5780}^{15\cdot} - 48\cdot9°$ ($c = 4\cdot871$, $l = 1$) in pyridine (Found: C, 61·3; H, 6·8; N, 11·9. $C_{12}H_{16}O_3N_2$ requires C, 61·0; H, 6·8; N, 11·9%).

The conversion of $D(-)$-valinol into α-bromoisobutylamine was carried under somewhat milder conditions than those employed for the $L(+)$-isomeride: the hydrochloride (0·5 g.) was heated with glacial acetic acid (10 c.c.), saturated with hydrogen bromide at $- 8°$, for only 5 hours at 70—75°, but under these conditions the replacement of the hydroxyl group was incomplete. The product from the catalytic reduction consisted of a mixture of unchanged valinol hydrochloride and $(-)$-*α-methylisobutylamine hydrochloride*. The last-named compound was separated by crystallisation from acetone and had $[\alpha]_{5461}^{21\cdot} - 3\cdot4°$ ($c = 3\cdot55$, $l = 1$) in water (Found: Cl, 28·5%); the p-*nitrobenzoyl* derivative, m. p. 112·5°, gave $[\alpha]_{5461}^{15\cdot} + 55\cdot8°$ ($c = 3\cdot664$, $l = 1$) in pyridine (Found: C, 61·1; H, 6·6; N, 11·9%).

Conversion of $L(+)$-*Alanine into* $(+)$-β-*Hydroxy-α-methylisobutylamine.*—Benzoylalanine was resolved by the method of Pope and Gibson (*loc. cit.*) and furnished $L(+)$-alanine, which had $[\alpha]_{5461}^{20\cdot} + 11\cdot1°$ ($c = 8\cdot87$, $l = 2$) in water, and was esterified in the usual manner. $L(+)$-Alanine ethyl ester hydrochloride (10·3 g.) was added in portions, during 15 minutes, to a solution of methylmagnesium iodide prepared from methyl iodide (57 g.; 6 mols.) in ether (400 c.c.), the mixture being mechanically stirred and heated to boiling for 3 hours. After decomposition with water (150 c.c.), the ethereal solution was decanted, and volatile bases were then removed from the residual sludge of magnesium hydroxide by the addition of sodium hydroxide and distillation in steam. The crude product, obtained by neutralising the distillate with hydrochloric acid, followed by evaporation, was freed from ammonium chloride by solution in hot butyl alcohol and precipitation with ether. $(+)$-β-*Hydroxy-α-methylisobutylamine hydrochloride* crystallised from acetone in long prismatic needles, m. p. 136°, and gave $[\alpha]_{5461}^{21\cdot} + 5\cdot6°$ ($c = 4\cdot14$, $l = 2$) in water (Found: N, 9·9; Cl, 25·8. $C_5H_{13}ON,HCl$ requires N, 10·0; Cl, 25·4%). Although the hydrochloride had a rotation somewhat lower than that of the optically pure compound obtained by the resolution of the inactive alcohol, on benzoylation in the presence of aqueous sodium hydroxide in the usual manner it yielded a N-*monobenzoyl* derivative, which crystallised from benzene–light petroleum in voluminous clusters of long needles, m. p. 116° (Found: C, 69·9; H, 8·4; N, 6·8. $C_{12}H_{17}O_2N$ requires C, 69·5; H, 8·3; N, 6·8%), and had the full activity $[\alpha]_{5461}^{20\cdot} - 17\cdot2°$ ($c = 5\cdot20$, $l = 1$) in pyridine and $[\alpha]_{5461}^{21\cdot} + 8\cdot1°$ ($c = 4\cdot81$, $l = 1$) in alcohol.

Preparation and Reduction of Inactive β-*Hydroxy-α-methylisobutylamine.*—The amino-alcohol was prepared by the interaction of inactive alanine ethyl ester hydrochloride (1 mol.) and methylmagnesium iodide (6 mols.) in ethereal solution, and isolated as the hydrochloride in a similar manner to that described above for the (+)-isomeride. The best yields (60—66%) were obtained by heating the reaction mixture for only 30 minutes after the addition of the ester hydrochloride, and also by filtering the aqueous solution from the magnesium hydroxide before the amino-alcohol was distilled in steam (if the magnesium hydroxide is not removed, the crude hydrochloride contains a considerable amount of ammonium chloride). β-*Hydroxy-α-methylisobutylamine hydrochloride* crystallised from aqueous acetone in small hard prisms containing

water of crystallisation (Found : loss on drying at 80° in a vacuum, 11·5. Found for the dried material : N, 8·7; Cl, 25·5. $C_8H_{19}ON,HCl,H_2O$ requires loss 11·4%. $C_8H_{19}ON,HCl$ requires N, 8·9; Cl, 25·4%) : the anhydrous salt had m. p. 117°. The N-*monobenzoyl* derivative crystallised in long slender needles, m. p. 96° (Found : C, 69·7; H, 8·6; N, 6·6. $C_{12}H_{17}O_2N$ requires C, 69·5; H, 8·3; N, 6·7%).

The reduction of β-hydroxy-α-methyl*iso*butylamine was effected by treating the hydrochloride with phosphorus pentachloride in chloroform solution, followed by catalytic reduction in a similar manner to that described below in the case of the active isomerides; the resulting α-methyl*iso*butylamine hydrochloride was identical with that obtained by the reduction of valinol (m. p. and mixed m. p. 203°) (Found : N, 11·5; Cl, 28·6%).

*Resolution of β-Hydroxy-α-methyl*iso*butylamine.*—(+)-Tartaric acid (13 g.) was dissolved in an aqueous solution (1300 c.c.) of the inactive amino-alcohol, prepared by distilling the hydrochloride (12 g.) with a slight excess of sodium hydroxide. The gummy residue obtained by evaporating the solution under reduced pressure was dissolved in alcohol (150 c.c.) and filtered from a small amount of ammonium hydrogen tartrate which separated. On the addition of acetone (400 c.c.), the solution deposited (over-night in the ice-chest) (+)-β-*hydroxy-α-methyl*iso*butylamine* (+)-*tartrate*, which was obtained in a pure condition by crystallisation from alcohol (200 c.c. of 96%). It formed long hard prisms (8 g.), containing water of crystallisation, which was removed by heating at 50° in a vacuum. The anhydrous salt had m. p. 166—167° (sintering at 161°), $[\alpha]_{5461}^{18°} + 22·2°$ ($c = 5·15, l = 2$) in water (Found : C, 43·0; H, 7·7; N, 5·6. $C_9H_{19}O_7N$ requires C, 42·7; H, 7·6; N, 5·5%). The *hydrochloride* was prepared from the tartrate by steam distillation with aqueous sodium hydroxide, followed by neutralisation and evaporation of the distillate. It had m. p. 140°, $[\alpha]_{5461}^{19°} + 6·1°$, $[\alpha]_{5780}^{19°} + 5·4°$ ($c = 4·21, l = 2$) in water (Found : N, 10·3; Cl, 25·4%). The N-*monobenzoyl* derivative, m. p. 116°, gave $[\alpha]_{5461}^{21°} + 8·3°$ ($c = 5·01, l = 1$) in alcohol and $[\alpha]_{5461}^{21°} - 16·8°$ ($c = 4·96, l = 1$) in pyridine (Found : C, 69·7; H, 8·3; N, 6·7%).

(−)-β-*Hydroxy-α-methyl*iso*butylamine hydrogen* (+)-*tartrate* was isolated from the first alcoholic mother-liquor from the crystallisation of the preceding tartrate by addition of acetone (800 c.c.), filtration from a further small crop which separated over-night, and concentration of the solution to 250 c.c. It formed voluminous aggregates of slender felted needles, which on recrystallisation from acetone–alcohol had $[\alpha]_{5461}^{16°} + 15·6$ ($c = 4·84, l = 2$) in water (Found : loss on drying at 100° in a vacuum, 6·6; N, 5·2. $C_9H_9O_7N,H_2O$ requires loss, 6·6; N, 5·2%) : the anhydrous salt had m. p. 122° (decomp.). Although the rotation remained unaltered on further crystallisation, the tartrate was not quite optically pure, since the *hydrochloride*, m. p. 138—139° (Found : Cl, 25·4%), prepared from it by distillation in the usual manner, had, after several crystallisations from alcohol–di*iso*propyl ether, a somewhat lower rotation, $[\alpha]_{5461}^{20°} - 5·5°$ ($c = 5·06, l = 2$), in water than that of the (+)-isomeride. The N-monobenzoyl derivative crystallised from benzene–light petroleum in long needles, m. p. 116·5°, and had $[\alpha]_{5461}^{21°} + 17·7°$, $[\alpha]_{5780}^{21°} + 15·2°$ ($c = 4·99, l = 1$) in pyridine, and $[\alpha]_{5461}^{19°} - 8·0°$ ($c = 4·85, l = 1$) in alcohol.

Reduction of (+)- *and* (−)-β-*Hydroxy-α-methyl*iso*butylamines.*—Phosphorus pentachloride (3·5 g.) was added in portions during 10 minutes to the (+)-amino-alcohol hydrochloride (2·5 g. having $[\alpha]_{5461}^{19°} + 6·1°$), suspended in chloroform (25 c.c.), and the solution then heated under reflux for a further 10 minutes. After removal of the chloroform and phosphorus oxychloride under reduced pressure, the crystalline residue was dissolved in methyl alcohol (20 c.c.) and catalytically reduced at the ordinary temperature and pressure in the presence of palladised charcoal (2 g. containing 30% of the metal). After filtration from the catalyst, the solution was basified with sodium hydroxide, distilled, and the (−)-α-methyl*iso*butylamine isolated from the distillate as the *hydrochloride* (1·2 g.), which after crystallisation from acetone had m. p. 201—204° (sintering at 195°), $[\alpha]_{5461}^{20°} - 1·65$ ($c = 4·96, l = 2$) in water (Found : N, 11·3; Cl, 28·5), and gave a p-*nitrobenzoyl* derivative, m. p. 107—108° (Found : C, 60·7; H, 6·7; N, 11·6%), having a lower rotation, $[\alpha]_{5461}^{17°} + 44·1$ ($c = 4·817, l = 1$), in pyridine than that of the *p*-nitrobenzoyl derivatives obtained by the reduction öf the active valinols. In a second experiment in which the (+)-amino-alcohol hydrochloride (2·8 g.) was gradually added, with cooling, to the pentachloride (4·2 g.) in chloroform (15 c.c.), and the mixture then shaken for 30 minutes at room temperature, the intermediate product was isolated by evaporating the solution under diminished pressure, dissolving the residue in alcohol, and precipitating the product with ether. From the analytical results, and also from its behaviour on reduction, it appears to consist of a mixture of the chloro-amine (XII) and the unsaturated amine (XIII). After catalytic reduction in dilute hydrochloric solution, it gave (−)-α-methyl*iso*butylamine hydrochloride, having $[\alpha]_{5461}^{20°} - 2·1°$ ($c = 4·72, l = 2$) in water : this yielded a p-*nitrobenzoyl*

derivative, the rotation of which was raised from $[\alpha]_{5461}^{20}$ + 47·4° to + 53·8° (c = 4·72, l = 2, in pyridine) after four crystallisations from benzene–light petroleum.

The reduction of (−)-β-hydroxy-α-methyl*iso*butylamine hydrochloride, having $[\alpha]_{5461}^{20}$ − 4·6°, was carried out in a similar manner : the resulting (+)-α-*methylisobutylamine hydrochloride* had $[\alpha]_{5461}^{17}$ + 2·4° (c = 5·18, l = 1) in water (Found : C, 48·6; H, 11·4. $C_5H_{13}N,HCl$ requires C, 48·6; H, 11·4%), and gave a p-*nitrobenzoyl* derivative, m. p. 112°, $[\alpha]_{5461}^{17}$ − 43·5° (c = 4·835, l = 1) in pyridine (Found : C, 61·1; H, 7·1; N, 11·9%).

Experiments with Benzoylalanine.—The methyl ester of inactive benzoylalanine, which has been prepared from the acid chloride by Max (*Annalen*, 1909, 369, 276), was obtained in excellent yield by saturating a solution of the acid (20 g.) in methyl alcohol (200 c.c.) with hydrogen chloride and allowing the solution to remain for 24 hours at the ordinary temperature. After removal of the excess of alcohol under reduced pressure, the residue was triturated with cold aqueous sodium carbonate and crystallised from aqueous alcohol; slender needles m. p. 81°. When heated for 8 hours with methylmagnesium iodide (6 mols.) in ethereal solution, it furnished the N-benzoyl derivative of β-hydroxy-α-methyl*iso*butylamine (m. p. and mixed m. p. 96°. Found : N, 6·6%) in 80% yield. Hydrolysis, accompanied by elimination of ammonia, occurred when the benzoyl derivative was heated under reflux with alcoholic potassium hydroxide (60 c.c. of 0·5N) for 14 hours : the amino-alcohol was isolated as the hydrochloride in the usual manner, the yield being only 8%. Attempts to convert the amino-alcohol into N-benzoyl-α-methyl*iso*butylamine under various conditions, by treatment with hydrobromic acid, thionyl chloride, and phosphorus pentachloride, followed by reduction both catalytically and otherwise, were unsuccessful.
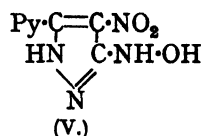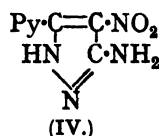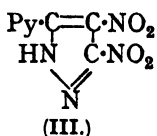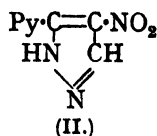
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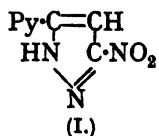
90. *Pyridylnitropyrazole. Part II. Derivatives of* 4-*Nitro-*5-*pyridyl-pyrazole.*

By Hakon Lund.

In Part I (J., 1933, 686) it was shown that the by-product formed when nicotine is oxidised with nitric acid (Gough and King, J., 1931, 2968; 1933, 350; King, J., 1932, 2768) is 3-nitro-5-(3′-pyridyl)pyrazole (I), and this structure has been confirmed by Clemo and Holmes (J., 1934, 1739). The isomeric 4-nitro-5-pyridylpyrazole (II) is obtained by nitration of 5-pyridylpyrazole; a number of its derivatives are now described.

(I), on nitration, yields a *dinitro*-derivative (III), but (II) cannot be nitrated under similar conditions. Reducing agents attack the nitro-group in the 3-position before attacking the other one. 4-*Nitro-*3-*amino-*5-*pyridylpyrazole* (IV) on deamination yields (II), a proof of the 3-position of the amino-group.

Py·C̲=CH   Py·C̲=C̲·NO₂   Py·C̲=C̲·NO₂   Py·C̲=C̲·NO₂   Py·C̲=C̲·NO₂
HN   C·NO₂   HN   CH   HN   C·NO₂   HN   C·NH₂   HN   C·NH·OH
  \ /   \ /   \ /   \ /   \ /
   N   N   N   N   N
 (I.)   (II.)   (III.)   (IV.)   (V.)

The series of reactions (I) ⟶ (III) ⟶ (IV) ⟶ (II) is the most advantageous way of preparing (II).

Reduction of (III) with stannous chloride without heating leads, not to the amine (IV), but to 4-*nitro-*3-*hydroxylamino-*5-*pyridylpyrazole* (V), which is remarkably stable in acid solution and is oxidised in alkaline solution to the corresponding *azoxy*-compound by air or potassium ferricyanide.

In acid solution bromic acid oxidises (V) to the corresponding nitroso-compound, which is green in acid solution and light yellow in the solid state. It has been isolated as the *perchlorate* because the free substance seems to be amorphous. In acid solution it oxidises the iodide ion to free iodine and is thereby reduced to (V). On reduction of (V) in hot sodium hydroxide solution with hydrogen sulphide, (IV) is formed, indicating the 3-position of the hydroxylamino-group. (V) is also formed when (III) is reduced by zinc dust in

ammoniacal solution. For the preparation of (V) this procedure has the disadvantage that in order to avoid oxidation to the azoxy-compound the process should be carried out in an oxygen-free atmosphere.

(IV) can be diazotised. The diazonium salts in aqueous solution can be heated to 70—80° without marked decomposition. The dry salts explode, the *perchlorate* violently, when heated. Some of the diazo-reactions proceed normally, but others take an unexpected course; *e.g.*, when a diazo-salt is added to aqueous ammonia, nitrogen is evolved and the 3-amine is formed in good yield (normally, bisdiazoimides are produced). These reactions are being studied in greater detail and the results will be published later.

Sodium hydrosulphite reduces the dinitro-compound (III) in alkaline solution to 3 : 4-diamino-5-pyridylpyrazole, isolated as a colourless *dihydrochloride*. The free base is very soluble in water and is oxidised by air.

<div align="center">EXPERIMENTAL.</div>

3 : 4-*Dinitro-5-pyridylpyrazole* (III).—3-Nitro-5-pyridylpyrazole (25 g.), dissolved in concentrated sulphuric acid (60 c.c.) by gentle heating, is treated with nitric acid (*d* 1·50, 25 c.c.), the mixture heated on the steam-bath for 30 minutes, cooled and poured into cold water (500 c.c.), concentrated aqueous ammonia added until the precipitate formed is redissolved, and the solution acidified with acetic acid. The yellow product is filtered off with suction and washed with water. 3 : 4-*Dinitro-5-pyridylpyrazole*, obtained pure and in quantitative yield, decomposes at 230° (Found : C, 40·9; H, 2·05; N, 29·6. $C_8H_5O_4N_5$ requires C, 40·85; H, 2·1; N, 29·8%).

The substance is soluble in aqueous ammonia even in presence of ammonium salts, in contrast with the initial material. It dissolves in hot dilute hydrochloric acid and, on cooling, a *hydrochloride* crystallises (Found : Cl, 13·2. $C_8H_5O_4N_5$,HCl requires Cl, 13·1%).

4-*Nitro-3-amino-5-pyridylpyrazole* (IV).—The moist preparation of (III) is dissolved in water (500 c.c.) containing sodium hydroxide (15 g.) and reduced at about 90° with hydrogen sulphide. The solution instantly becomes dark red and when it is saturated with the gas 4-*nitro-3-amino-5-pyridylpyrazole* has separated quantitatively in fine needles. After being washed with water the amine is pure enough for use, but it may be recrystallised from alcohol or dissolved in very dilute sodium hydroxide solution and reprecipitated by carbon dioxide. Yield, 26 g. or 97% (Found : C, 46·8; H, 3·5; N, 34·1. $C_8H_7O_2N_5$ requires C, 46·8; H, 3·4; N, 34·1. Found for the *hydrochloride* : Cl, 14·7. $C_8H_7O_2N_5$, HCl requires Cl, 14·7%). The amine is insoluble in aqueous ammonia, but dissolves in aqueous sodium hydroxide and in dilute hydrochloric acid, giving an orange and a yellow solution respectively. The acetyl derivative melts at 175°.

The diazonium nitrate. When (IV) is diazotised in 4N-nitric acid (4 mols.) without cooling, a clear solution is obtained which deposits crystals of the *diazonium nitrate* when cooled in ice-water (yield, 80%). The salt is recrystallised from water below 70° [Found : N (micro-Dumas), 35·0. $C_8H_5O_5N_7$ requires N, 35·1%].

The *diazonium perchlorate*, which is rather slightly soluble in water, is prepared by diazotising (IV) in 4N-hydrochloric acid, filtering the luke-warm solution, and adding 70% perchloric acid; the perchlorate soon crystallises. The dry salt can be ground in a mortar without exploding, but when knocked with a hammer or when heated to 160° it explodes with great violence (Found : N, 26·3. $C_8H_5O_6N_6Cl$ requires N, 26·55%).

4-*Nitro-5-pyridylpyrazole.*—The amine (IV) (41 g.) is diazotised in hydrochloric acid (90 c.c + 50 c.c. of water) by addition of sodium nitrite (19 g.). The paste of the diazonium chloride formed is poured into boiling alcohol (500 c.c.); a moderate evolution of nitrogen takes place; after 20 minutes' boiling the alcohol is evaporated, water added until the hydrochloride redissolves, and the filtered solution made ammoniacal and then slightly acid with acetic acid. The 4-nitro-5-pyridylpyrazole obtained has m. p. 220° after recrystallisation from water (yield, 28 g.) (Found : N, 29·5. Calc. for $C_8H_6O_2N_4$: N, 29·6%).

4-*Nitro-3-hydroxylamino-5-pyridylpyrazole* (V).—3 : 4-Dinitro-5-pyridylpyrazole (III) (12 g.) is dissolved in hydrochloric acid (20 c.c. + 25 c.c. of water), a solution of stannous chloride (25 g.) in concentrated hydrochloric acid (25 c.c.) rapidly added, and the mixture cooled in running water. When the reaction is over, the solution is cooled in ice-water, and concentrated hydrochloric acid (10 c.c.) added. The yellow crystalline product is washed with ice-cold 20% hydrochloric acid, dissolved in hot water, and, after addition of concentrated hydrochloric acid, cooled in ice (yield of the hydrochloride, 10 g.). The *hydroxylamino*-compound, obtained in quantitative yield from an aqueous solution of the hydrochloride and excess of sodium acetate,

decomposes at 177—178° (Found : C, 43·45; H, 3·4; N, 31·5. $C_8H_7O_5N_5$ requires C, 43·4; H, 3·2; N, 31·6%). It is a yellow substance which forms yellow solutions in acids, orange solutions in weak bases, and intensely red-violet (cherry) solutions in strong bases. It is reduced in hot alkaline solution to (IV) by hydrogen sulphide.

4-Nitro-3-azoxy-5-pyridylpyrazole.—Air or oxygen is passed through a solution of (V) in dilute aqueous sodium hydroxide until the violet-red colour has disappeared; a yellow compound (the sodium salt of the azoxy-compound) crystallises if the solution is not very dilute. Acetic acid is added, and the *azoxy*-compound is obtained in quantitative yield. It is purified by dissolving it in hot dilute hydrochloric acid and cooling. The hydrochloride is soluble in water, but when it is boiled with about 50 parts of water it is completely hydrolysed and the free base separates as an orange-yellow, very finely divided substance (Found : C, 45·4; H, 2·5; N, 28·0. $C_{16}H_{10}O_5N_{10}$ requires C, 45·5; H, 2·4; N, 33·2%).

4-Nitro-3-nitroso-5-pyridylpyrazole Perchlorate.—A solution of the hydrochloride of (V) (5·1 g.) in dilute hydrochloric acid becomes green on addition of potassium bromate (1·1 g.). After 10 minutes, sodium acetate in excess is added, the nitroso-compound filtered off and dissolved in dilute lukewarm hydrochloric acid, and 70% perchloric acid added; the *perchlorate* crystallises. Neither the free nitroso-compound nor the hydrochloride could be obtained crystalline. In an attempt to recrystallise the perchlorate from alcohol the smell of aldehyde was noticed. The perchlorate explodes on heating and therefore no combustion was made (Found : N, 21·9. $C_8H_6O_7N_5Cl$ requires N, 21·9%).

The nitroso-perchlorate liberates iodine from an acid solution of potassium iodide; 0·0858 g. gave an amount corresponding to 5·30 c.c. 0·1N-sodium thiosulphate (calc. for 2 equivs. of iodine per mol., 5·35 c.c.). After the titration an excess of sodium hydroxide was added, whereby the solution became intensely red-violet, indicating the presence of (V).

3 : 4-Diamino-5-pyridylpyrazole.—To a solution of the dinitro-compound (III) (23·5 g.) in aqueous sodium hydroxide (8 g. in 300 c.c. of water) at 90°, sodium hydrosulphite (about 75 g.) is added in small portions, a little sodium hydroxide being added to keep (III) in solution. The hot, almost colourless solution is treated with an excess of concentrated hydrochloric acid, filtered from sulphur, and evaporated to dryness under reduced pressure. Alcohol (200 c.c.) and potassium carbonate (50 g.) are added to the residue and the mixture is boiled under reflux for 2 hours. After filtration the solid mass is washed with alcohol (100 c.c.), and to the combined filtrate and washings is added an excess of alcoholic hydrogen chloride (concentrated hydrochloric acid may be used without greatly diminishing the yield). The *diamine dihydrochloride* (24·8 g.) is immediately precipitated. It can be recrystallised from hot 25% hydrochloric acid by addition of alcohol; the colourless crystals, however, soon again acquire a brownish colour in contact with air (Found : N, 28·5; Cl, 28·6. $C_8H_7N_5,2HCl$ requires N, 28·2; Cl, 28·6%).

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91. *Studies on the Michael Reaction. Part I. The Condensation of Ethyl Benzylmalonate with Ethyl Fumarate.*

By H. N. RYDON.

THE view that the sodio-derivatives of alkylcyanoacetic esters underwent partition in the

sense $R\!\cdot\!\overset{\overset{\displaystyle Na}{\frown}}{C(CN)\!\cdot\!CO_2Et}$ during the Michael reaction was first advanced by Thorpe (J., 1900, 77, 923). Michael and Ross (*J. Amer. Chem. Soc.*, 1930, 52, 4600) obtained evidence for a similar partition of alkylmalonic esters in the presence of one molecular proportion of sodium ethoxide. Holden and Lapworth (J., 1931, 2370) challenged these conclusions, pointing out that this apparent partition could equally well be explained by a migration of the carbethoxy- or cyano-group and postulating an intermediate cyclisation of the Dieckmann type to account for this. Although Michael and Ross replied to this criticism (*J. Amer. Chem. Soc.*, 1932, 54, 407; 1933, 55, 1632), the point was left open to doubt, since no evidence was put forward that could not be explained by the mechanism of Holden and Lapworth.

Connor (*ibid.*, 1933, 55, 4597) attempted to throw light on the problem by studying

the Michael reaction with phenylmalonic ester, supposing the phenyl group to be particularly favourable to partition in the manner proposed by Thorpe; his work was fruitless, since no condensation could be brought about. Recently, however, Duff and Ingold (J., 1934, 87), by the condensation of ethyl fumarate and of ethyl α-bromosuccinate with ethyl benzylmalonate, obtained two isomeric tetracarboxylic esters, which, on hydrolysis and decarboxylation, gave rise to a pair of, presumably, stereoisomeric phenylbutanetricarboxylic acids. Inasmuch as the intermediate tetracarboxylic ester (I) contains only one asymmetric carbon atom, only one inactive isomeride is capable of existence (Duff and Ingold, *loc. cit.*, p. 88, incorrectly postulate the existence of two forms). It appeared, therefore, to be of interest to repeat this work, in order to elucidate the nature of these isomeric esters and so throw further light on this important problem.

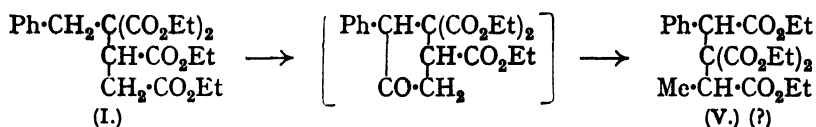The experimental results are outlined in the following scheme :

$$
\begin{bmatrix}
Ph\cdot CH_2\cdot CH(CO_2Et)_2 \\
+ \\
\underset{|}{C}H\cdot CO_2Et \\
CO_2Et\cdot CH
\end{bmatrix}
\xleftarrow{\ NaOEt\ }
\begin{array}{c}
Ph\cdot CH_2\cdot \underset{|}{C}(CO_2Et)_2 \\
{}^*CH\cdot CO_2Et \\
CH_2\cdot CO_2Et \\
(I.)
\end{array}
\xrightarrow{\ H_2SO_4\ }
\begin{array}{c}
Ph\cdot CH_2\cdot \overset{*}{C}H\cdot CO_2H \\
{}^*CH\cdot CO_2H \\
CH_2\cdot CO_2H \\
(II.)\ m.\ p.\ 190—191°.
\end{array}
$$

(with diagonal arrow labelled **NaOEt + MeI** from (I) to (III))

(from (II) downward arrow labelled **H₂O**)

$$
\begin{array}{c}
Ph\cdot CH_2\cdot \underset{|}{C}H\cdot CO_2H \\
CO_2H\cdot \underset{|}{C}H \\
Me\cdot CH\cdot CO_2H \\
(IV.)\ m.\ p.\ 181—183°.
\end{array}
\xleftarrow{\ H_2SO_4\ }
\begin{array}{c}
Ph\cdot CH_2\cdot \underset{|}{C}H\cdot CO_2Et \\
CO_2Et\cdot \underset{|}{C}H \\
Me\cdot C(CO_2Et)_2 \\
(III.)
\end{array}
\qquad
\begin{array}{c}
Ph\cdot CH_2\cdot \underset{|}{C}H\cdot CO \\
CO_2H\cdot \underset{|}{C}H \quad \rangle O \\
CH_2\cdot CO \\
(VII.)
\end{array}
$$

(between (III) and (V): left arrow labelled **Na in C₆H₆ + MeI**, right arrow labelled **NaOEt + MeI**)

(between (VII) and (VI): arrows labelled **+H₂O** / **−H₂O**)

$$
\begin{array}{c}
Ph\cdot CH_2\cdot \overset{*}{C}H\cdot CO_2Et \\
CO_2Et\cdot \overset{*}{C}H \\
CH(CO_2Et)_2 \\
(V.)
\end{array}
\xrightarrow{\ H_2SO_4\ }
\begin{array}{c}
Ph\cdot CH_2\cdot \overset{*}{C}H\cdot CO_2H \\
CO_2H\cdot \overset{*}{C}H \\
CH_2\cdot CO_2H \\
(VI)\ m.\ p.\ 175°.
\end{array}
$$

The constitution of the product obtained from ethyl α-bromosuccinate and ethyl benzylmalonate is not open to serious doubt. Condensation by means of sodium ethoxide yielded the tetracarboxylic ester (I); this, on acid hydrolysis, afforded a δ-phenyl-*n*-butane-αβγ-tricarboxylic acid (II), m. p. 190—191°, undoubtedly identical with the acid, m. p. 187—190°, obtained in a similar manner by Duff and Ingold (*loc. cit.*). The ester (I) could not be hydrolysed to the parent tetracarboxylic acid owing to the ease with which decarboxylation occurred. It was readily methylated by means of sodium ethoxide and methyl iodide, yielding a mixture of products. The lower-boiling products were identified as ethyl fumarate and ethyl benzylmethylmalonate, evidently produced by a retrograde Michael reaction, followed by methylation of the ethyl benzylmalonate so produced. The principal product of the reaction was *ethyl δ-phenyl-α-methyl-*n*-butane-αα-trans-βγ-tetracarboxylate* (III). On boiling with acid this was smoothly hydrolysed and decarboxylated to *δ-phenyl-α-methyl-*n*-butane-α-trans-βγ-tricarboxylic acid* (IV), m. p. 178—182°. In this case, also, the tetracarboxylic acid could not be obtained in a pure condition. Attempted methylation of the ester (I) with " molecular " sodium in benzene in place of sodium ethoxide was unsuccessful. No product of the molecular complexity of the methylated ester (III) could be isolated, the only substance obtained being a comparatively small amount of a mixture of isomeric malonic acids, $C_{11}H_{12}O_4$, one component of which was identified as benzylmethylmalonic acid. Extensive and deep-seated decomposition occurred during the reaction and the conclusion may safely be drawn that the ester (I) contains no hydrogen atom normally replaceable by sodium—an additional confirmation of the structure

Condensation of ethyl fumarate with ethyl benzylmalonate in the presence of one molecular proportion of sodium ethoxide yielded a tetracarboxylic ester (V); this, on acid hydrolysis, readily afforded δ-phenyl-*n*-butane-α-*trans*-βγ-tricarboxylic acid (VI), m. p. 175°, evidently the same as that obtained by Duff and Ingold (*loc. cit.*; m. p. 168°). Since no other isomeride could be isolated, the configuration ascribed to this compound, and to its derivatives described below, follows from its production from ethyl fumarate. Once again the tetracarboxylic acid was too unstable to permit of satisfactory purification. The ester (V), on treatment with methyl iodide in the presence of sodium ethoxide, yielded certain amounts of retrogression products corresponding to the possible presence of not more than 16% of (I) in (V), together with ethyl δ-phenyl-α-methyl-*n*-butane-αα-*trans*-βγ-tetracarboxylate (III). The same ester was produced in good yield when "molecular" sodium in benzene was substituted for sodium ethoxide in alcohol; this difference in behaviour with sodium affords strong evidence for the view that the ester (V) differs from (I) in possessing a hydrogen atom normally, and readily, replaceable by sodium. That the methylated ester (III) produced by these methods was identical with that obtained from the ester (I) was easily demonstrated, acid hydrolysis yielding the same δ-phenyl-α-methyl-*n*-butane-α-*trans*-βγ-tricarboxylic acid (IV), m. p. 181—183° and 180—181°, respectively; the identity was confirmed by mixed melting points.
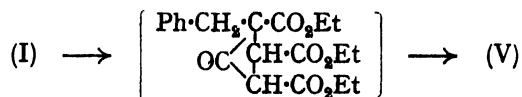
The marked difference in behaviour of the esters (I) and (V) towards sodium points clearly to a structural difference, the benzyl group having, in some manner yet to be determined, migrated from the α- to the γ-carbon atom during the Michael addition. If this migration occurs by the "Dieckmann mechanism" of Holden and Lapworth (*loc. cit.*), there are only two possibilities which need be considered.

The first, which is unlikely, but rendered possible by the activating influence of the phenyl group (cf. the formation of a sodio-derivative by phenylacetonitrile), is outlined in the scheme :

$$
\begin{array}{ccc}
\begin{array}{l}\text{Ph·CH}_2\text{·C(CO}_2\text{Et)}_2\\ \text{CH·CO}_2\text{Et}\\ \text{CH}_2\text{·CO}_2\text{Et}\end{array}
&\longrightarrow&
\left[\begin{array}{l}\text{Ph·CH·C(CO}_2\text{Et)}_2\\ \text{CH·CO}_2\text{Et}\\ \text{CO·CH}_2\end{array}\right]
&\longrightarrow&
\begin{array}{l}\text{Ph·CH·CO}_2\text{Et}\\ \text{C(CO}_2\text{Et)}_2\\ \text{Me·CH·CO}_2\text{Et}\end{array}\\
\text{(I.)} & & & & \text{(V.) (?)}
\end{array}
$$

On this hypothesis the acids (II) and (VI) should be structurally different, (II) being a benzyltricarballylic acid and (VI) a phenylmethyltricarballylic acid.

The second, and more likely, mechanism is the following :

$$
\text{(I)} \longrightarrow \left[\begin{array}{l}\text{Ph·CH}_2\text{·C·CO}_2\text{Et}\\ \text{OC}\diagdown\text{CH·CO}_2\text{Et}\\ \text{CH·CO}_2\text{Et}\end{array}\right] \longrightarrow \text{(V)}
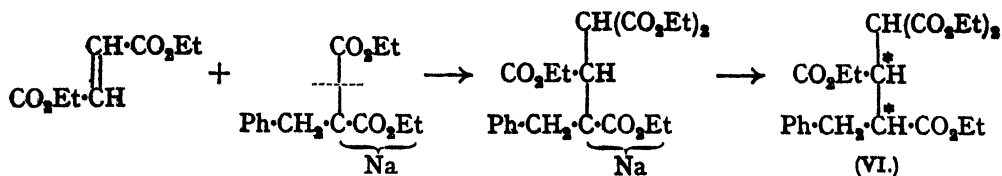$$

In this case the acids (II) and (VI) should be identical, since stereoisomerism, as already pointed out (p. 421), is not possible owing to the presence of only one asymmetric carbon atom in (I). This hypothesis is thus not consistent with the experimental facts and must be rejected.

The acids (II) and (VI) both yielded the same anhydro-acid (VII), m. p. 110—112° (Thiele and Meisenheimer, *Annalen*, 1899, **306**, 247; Duff and Ingold, *loc. cit.*). This anhydro-acid was readily hydrolysed back to the acid (VI), m. p. 176°, identified by mixed m. p. The acids are therefore stereoisomeric, and the first hypothesis advanced above must also be rejected. The configuration of the acid (II) is uncertain; it may be either the *cis*-compound or a mixture of the *cis*- and the *trans*-; such mixtures are often exceedingly difficult to separate by crystallisation and at times behave like pure substances. A parallel for the production of only one compound is afforded by the work of Henstock and Sprankling (J., 1907, **91**, 355), who obtained only one, apparently homogeneous, ααα'-trimethyltricarballylic acid by a similar reaction.
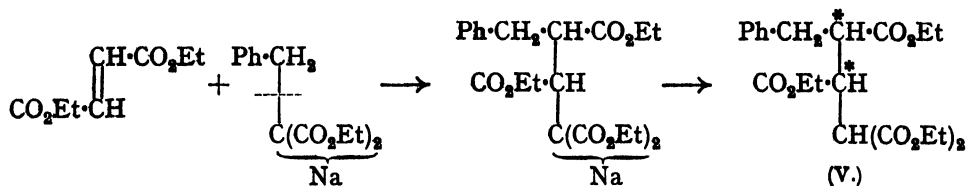
The only way in which ethyl benzylmalonate can react with ethyl fumarate so as to

preserve the two asymmetric centres necessary for the production of this stereoisomeride is by fission at the moment of addition. This may occur in two ways—first, as follows :

$$\begin{array}{c} \text{CH·CO}_2\text{Et} \\ \| \\ \text{CO}_2\text{Et·CH} \end{array} + \begin{array}{c} \text{CO}_2\text{Et} \\ | \\ \text{Ph·CH}_2\text{·C·CO}_2\text{Et} \\ \underbrace{\qquad}_{\text{Na}} \end{array} \longrightarrow \begin{array}{c} \text{CH(CO}_2\text{Et)}_2 \\ \text{CO}_2\text{Et·CH} \\ \text{Ph·CH}_2\text{·C·CO}_2\text{Et} \\ \underbrace{\qquad}_{\text{Na}} \end{array} \longrightarrow \begin{array}{c} \text{CH(CO}_2\text{Et)}_2 \\ \text{CO}_2\text{Et·CH} \\ \text{Ph·CH}_2\text{·CH·CO}_2\text{Et} \\ (\text{VI.}) \end{array}$$

In this case, although two asymmetric carbon atoms are produced, they are not the carbon atoms originally present in the ethyl fumarate; there is no reason for anticipating the formation of the *trans*-ester in preference to the *cis*-; this hypothesis thus demands that (II) and (VI) be identical; for this reason it must be rejected.

There remains only partition in the manner advanced by Thorpe, *viz.* :

$$\begin{array}{c} \text{CH·CO}_2\text{Et} \\ \| \\ \text{CO}_2\text{Et·CH} \end{array} + \begin{array}{c} \text{Ph·CH}_2 \\ | \\ \text{C(CO}_2\text{Et)}_2 \\ \underbrace{\qquad}_{\text{Na}} \end{array} \longrightarrow \begin{array}{c} \text{Ph·CH}_2\text{·CH·CO}_2\text{Et} \\ \text{CO}_2\text{Et·CH} \\ \text{C(CO}_2\text{Et)}_2 \\ \underbrace{\qquad}_{\text{Na}} \end{array} \longrightarrow \begin{array}{c} \text{Ph·CH}_2\text{·CH·CO}_2\text{Et} \\ \text{CO}_2\text{Et·CH} \\ \text{CH(CO}_2\text{Et)}_2 \\ (\text{V.}) \end{array}$$

In this case the two asymmetric carbon atoms formed are those derived from the ethyl fumarate; we should thus expect to obtain the *trans*-acid on hydrolysis, *i.e.*, the acids (II) and (VI) should be stereoisomeric. Since this has been shown to be the case, this hypothesis is the only one that can be accepted.

The anhydro-acid, reverting as it does to the *trans*-acid (VI), must be formed by the elimination of water from the α- and the γ-carboxyl group (which are necessarily in the *cis*-position), *i.e.*, it is α-benzyl-β-carboxyglutaric anhydride (VII, p. 421).

On the basis of the above reasoning it may be concluded that, in the condensation of ethyl benzylmalonate with ethyl fumarate, partition of the sodio-derivative of the malonic ester occurs in such a way that the sodium remains attached to the malonic residue. In this particular instance the reaction appears to proceed in this manner to the extent of at least 85%; whether this is general or whether, with other alkylmalonic esters, the alkyl group may remain attached wholly or partly (in the statistical sense) to the malonic residue is a matter for further experiment. It is perhaps significant that, whereas Auwers, Köbner, and von Meyenburg (*Ber.*, 1891, **24**, 2897) obtained an α-ethyltricarballylic acid, m. p. 147—148°, from ethyl fumarate and ethyl ethylmalonate, Jowett (*J.*, 1901, **79**, 1349) obtained another form (?) of the same acid, m. p. 157°, from ethyl bromoacetate and ethyl α-cyano-α'-ethylsuccinate, a pair of reactions analogous to those described in this paper; this work is being re-investigated with a view to determining the range of applicability of the above mechanism.

<div align="center">EXPERIMENTAL.</div>

Condensation of Ethyl Benzylmalonate with Ethyl α-Bromosuccinate.—The condensation, essentially by Duff and Ingold's method (*loc. cit.*), afforded a 45% yield of ethyl δ-phenyl-*n*-butane-αβγγ-tetracarboxylate (I), b. p. 203—209°/2·5 mm. (Duff and Ingold, *loc. cit.*, give b. p. 184—186°/0·6 mm.).

Hydrolysis. The ester (I) was hydrolysed by Duff and Ingold's method (*loc. cit.*); the product, which separated in almost theoretical yield on cooling, was recrystallised from acetic acid. The δ-phenyl-*n*-butane-αβγ-tricarboxylic acid (II) [Found : C, 58·6; H, 5·6; equiv., 88·3. Calc. for $C_{13}H_{14}O_6$ (tribasic) : C, 58·6; H, 5·2%; equiv., 88·7] obtained had m. p. 190—191° (decomp.) [Duff and Ingold, *loc. cit.*, record m. p. 187—190° (decomp.)], and was apparently homogeneous, all crops having similar m. p.'s.

The acid (II) on boiling with nitrobenzene for a few minutes, followed by precipitation with petroleum, yielded β-carboxy-α-benzylglutaric anhydride (VII) in long needles, m. p. 111—113°. This was also prepared, in good yield, by heating the acid at 200° for 30 minutes; recrystallised from benzene–petroleum, it formed rosettes of needles, m. p. 112°.

Methylation in alcoholic solution. 10·5 G. of the ester (I) were added to sodium ethoxide (from sodium, 0·575 g., and absolute alcohol, 20 c.c.), 3 c.c. (2 mols.) of methyl iodide added, and the mixture refluxed over-night. The neutral product was poured into water, acidified, and extracted with ether. Removal of the ether from the dried extract, followed by distillation, yielded (i) 2 g., b. p. 80—110°/1·5 mm., (ii) 2 g., b. p. 110—135°/1·5 mm., (iii) 3 g., b. p. 136—150°/ 1·5 mm., and (iv) 7 g. of *ethyl δ-phenyl-α-methyl-n-butane-αα-trans-βγ-tetracarboxylate* (III), b. p. 175—195°/1·5 mm. Fractions (i) and (iii) were identified as ethyl fumarate and ethyl benzylmethylmalonate respectively, and fraction (ii) as a mixture of the two, by hydrolysis to the parent acids, identified by mixed m. p. with authentic specimens.

Hydrolysis. 6·3 G. of the ester (III), prepared as above, were refluxed over-night with con-centrated sulphuric acid (6 c.c.), water (2 c.c.), and formic acid (19 c.c.). An almost theoretical yield of the crude product was obtained on cooling. Two recrystallisations from acetic acid yielded *δ-phenyl-α-methyl-n-butane-α-trans-βγ-tricarboxylic acid* (IV) in sheaves of thin pris-matic needles, m. p. 178—182° (decomp.) [Found : C, 59·7; H, 5·8; equiv., 94·3. $C_{14}H_{16}O_6$ (tribasic) requires C, 60·0; H, 5·7%; equiv., 93·3]. The m. p. of this product was depressed to 165—174° (decomp.) on admixture with the unmethylated acid (II).

Attempted methylation in benzene solution. 0·77 G. of pulverised sodium was treated with a solution of 14 g. of the ester (I) in 50 c.c. of benzene. A slight reaction occurred at first, but this rapidly abated; the sodium was brought into solution only by long boiling under reflux, yielding a deep brown solution with a greenish fluorescence. 10 G. (2 mols.) of methyl iodide were added to this and the mixture was refluxed; after 48 hours the still strongly alkaline mixture was poured into water and extracted with benzene. Distillation of the dried extract yielded 6 g. of a product, b. p. 140—170°/1—1·5 mm.; the large amount of residue decomposed vigorously, leaving a hard black mass, and was not further investigated.

The product was boiled under reflux over-night with a solution of 6·5 g. of potassium hydr-oxide in 13 c.c. of water. On dilution and acidification a good yield of crystalline material slowly separated. Recrystallisation from benzene–petroleum yielded splendid shining plates, m. p. 140° (decomp.), with considerable shrinking and softening at 129°. This mixture had the composition $C_{11}H_{12}O_4$ [Found : C, 63·8; H, 6·0; equiv., 100·3; M (Rast), 195. Calc. (dibasic) : C, 63·5; H, 5·8%; equiv., 104; M, 208]. It was undoubtedly a mixture of malonic acids, since, when heated at 160° for 15 minutes, it evolved much carbon dioxide, yielding an oily product distinguished from the original mixture by being very soluble in cold benzene. Re-fluxing with acetyl chloride for 30 minutes, removal of the acetyl chloride, etc., left an oily anhydride. This, heated at 150—180° with urea, yielded β-*phenyl-α-methylpropionamide* (Found : N, 8·9. $C_{10}H_{13}ON$ requires N, 8·6%), m. p. 106° after two recrystallisations from petroleum, identified by mixed m. p. with a sample prepared similarly from authentic benzyl-methylmalonic acid. The mixture of acids crystallised from benzene in stellate clusters of needles, and from water in beautiful compact prisms. All attempts to identify the other con-stituent were fruitless.

Condensation of Ethyl Benzylmalonate with Ethyl Fumarate.—The condensation, by Duff and Ingold's method (*loc. cit.*), with 1 mol. of sodium ethoxide, gave a 53% yield of ethyl δ-phenyl-*n*-butane-αα-*trans*-βγ-tetracarboxylate (V), as a thick yellow oil, b. p. 215—220°/1·5 mm. (the b. p., 204—208°/0·09 mm., recorded by Duff and Ingold, *loc. cit.*, is undoubtedly too high).

Hydrolysis. The ester (V) was hydrolysed as described by Duff and Ingold (*loc. cit.*); a good yield of the crude acid separated on cooling. Crystallisation from acetic acid afforded pure δ-phenyl-*n*-butane-α-*trans*-βγ-tricarboxylic acid (VI) as small prismatic needles, m. p. 175° (decomp.) [Duff and Ingold, *loc. cit.*, record m. p. 168° (decomp.)] [Found : C, 58·7; H, 5·5; equiv., 87·4. Calc. for $C_{13}H_{14}O_6$ (tribasic) : C, 58·6; H, 5·2%; equiv., 88·7]. No trace of any other isomeride could be isolated, successive crops having very similar m. p.'s. The m. p. of this product was depressed to 160—165° on admixture with the stereoisomeric acid (II).

The acid (VI), heated at 200° for 30 minutes, yielded a product, from which α-benzyl-β-carb-oxyglutaric anhydride (VII) was isolated in good yield by recrystallisation from benzene-petroleum, forming clusters of needles, m. p. 110—112°, not depressed on admixture with the anhydride produced from the acid (II).

This anhydride, on boiling with water, regenerated the acid (VI), m. p. 176° (decomp.) after one crystallisation from acetic acid. The m. p. was not depressed on admixture with other specimens of this acid, but was depressed to 165—172° (decomp.) on admixture with the acid (II).

Methylation in alcoholic solution. 10·5 G. of the ester (V) were added to sodium ethoxide from sodium, 0·575 g., and absolute alcohol, 20 c.c.), 2 c.c. (excess) of methyl iodide added, and

the mixture boiled under reflux over-night. The quite neutral product was poured into water and extracted with ether. Removal of the ether from the dried extract left an oil which, on distillation, yielded two fractions. The low fraction (1·5 g.), b. p. 110—160°/2 mm., yielded on hydrolysis a mixture of fumaric and benzylmethylmalonic acids (both identified by mixed m. p. with authentic samples) and was thus a mixture of their esters. The high-boiling fraction (8 g.), b. p. 170—190°/1 mm., consisted of ethyl δ-phenyl-α-methyl-*n*-butane-αα-*trans*-βγ-tetra-carboxylate (III), a thick yellow oil.

Hydrolysis. 3 G. of the ester (III), prepared as above, were refluxed with concentrated sulphuric acid (3 c.c.), water (3 c.c.), and formic acid (9 c.c.) for 20 hours. The rather tarry product was filtered from the cooled solution. Crystallisation from acetic acid yielded δ-phenyl-α-methyl-*n*-butane-α-*trans*-βγ-tricarboxylic acid (IV) in sheaves of prismatic needles, m. p. 181—183° (decomp.) [Found : C, 59·8; H, 5·7; equiv., 94·6. Calc. for $C_{14}H_{16}O_6$ (tribasic) : C, 60·0; H, 5·7% ; equiv., 93·3]. The m. p. was not depressed on admixture with the similar product obtained by methylation of the ester (I), but was depressed to 161—169° (decomp.) on admixture with the unmethylated acid (VI).

Alkaline hydrolysis of the ester (III) proceeded readily, but the product underwent decarboxylation with extraordinary ease, a single crystallisation from formic acid yielding the acid (IV), m. p. 180—182° (decomp.), identified by mixed m. p.

Methylation in benzene solution. 0·77 G. of pulverised sodium was treated with a solution of 14 g. of the ester (V) in 50 c.c. of benzene. Reaction was fairly vigorous in the cold and was completed by boiling under reflux for 4 hours. The resulting opalescent orange-red solution was treated with 10 g. (2 mols.) of methyl iodide. Reaction proceeded in the cold with deposition of sodium iodide and was completed by boiling under reflux over-night. The neutral product was poured into water, acidified, and extracted with benzene. Distillation of the dried extract afforded ethyl δ-phenyl-α-methyl-*n*-butane-αα-*trans*-βγ-tetracarboxylate (9·6 g.), b. p. 188—198°/2 mm.

Hydrolysis. 3·2 G. of the above ester were refluxed over-night with concentrated sulphuric acid (3 c.c.), water (3 c.c.), and formic acid (9 c.c.). The hot liquid was filtered from a little tar and cooled; 1·8 g. (90%) of crude product crystallised. Recrystallisation from acetic acid yielded δ-phenyl-α-methyl-*n*-butane-α-*trans*-βγ-tricarboxylic acid (IV), m. p. 180—181° (decomp.), not depressed on admixture with samples prepared in other ways (above and p. 424).

92. *An Easy Method for the Preparation of* l-*Xylose.*

By HERBERT APPEL.

AFTER Haworth (*J. Soc. Chem. Ind.*, 1933, **52**, 645) and Reichstein (*Helv. Chim. Acta*, 1933, **16**, 1019) and their respective co-workers had shown that *l*-xylose (or *l*-xylosazone) was a useful material for the synthesis of *l*-ascorbic acid, the author worked out, and completed in December, 1933, an easy method for the preparation of the sugar, previously accessible only by the complicated process of Fischer and Ruff (*Ber.*, 1900, **33**, 2145). Triethylidene sorbitol, prepared by treating sorbitol with paraldehyde and hydrochloric acid (compare Helferich and Appel, *Ber.*, 1931, **64**, 1841), lost one acetaldehyde group when heated with 50% acetic acid, yielding 1 : 2 : 3 : 4-*diethylidene sorbitol* (I). Oxidation of (I) with lead tetra-acetate produced diethylidene *l*-xylose (II) (not isolated), and after hydrolysis with dilute sulphuric acid *l*-xylose was obtained. Vargha has recently (*Ber.*, 1935, **68**, 18) prepared *l*-xylose by the similar method of oxidising 1 : 3-monobenzylidene sorbitol with lead tetra-acetate.

$$\begin{array}{cc} \text{O·CHMe·O} \quad \text{O·CHMe·O} & \text{O·CHMe·O} \quad \text{O·CHMe·O} \\ \text{CH}_2\text{———CH·CH———CH·CH(OH)·CH}_2\text{·OH} & \text{CH}_2\text{———CH·CH———CH·CHO} \\ \text{(I.)} & \text{(II.)} \end{array}$$

F F
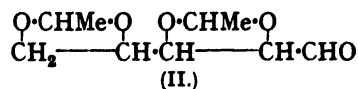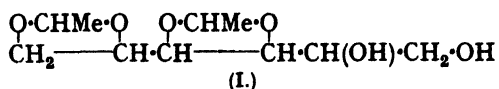
1 : 2 : 3 : 4-*Diethylidene Sorbitol.*—Sorbitol (50 g.) was shaken for 10 hours with paraldehyde (50 c.c.) and hydrochloric acid (17 c.c., *d* 1·19), chloroform (100 c.c.) added, the mixture washed successively with water, dilute aqueous sodium hydroxide, and water, and the chloroform-paraldehyde solution dried over calcium chloride and evaporated under diminished pressure. The residual thick syrup, consisting of triethylidene sorbitol (it could be obtained crystalline, m. p. 174—176°, but recrystallisation at this stage was wasteful and unnecessary), was dissolved in 50% acetic acid (300 c.c.) and heated for 50 minutes on the water-bath; the solvent was then removed quickly under diminished pressure at 70°. The residue was recrystallised from methyl alcohol, and addition of ether and light petroleum increased the yield (17 g.); m. p. 212—214°, $[\alpha]_D^{17}$ − 11·1° (*c* = 2·3 in water) (Found : C, 51·1; H, 7·7. $C_{10}H_{18}O_6$ requires C, 51·25; H, 7·75%).

β-*Tetra-acetyl* l-*Xylose.*—A mixture of diethylidene sorbitol (4 g.), lead tetra-acetate (8·6 g.), benzene (40 c.c.), and glacial acetic acid (20 c.c.) was left over-night with occasional shaking, the solvent then removed under diminished pressure, 2*N*-sulphuric acid (60 c.c.) added, and the mixture heated during 1½ hours on the water-bath. The filtered solution was nearly neutralised (litmus) with alkali (the free *l*-xylose can be obtained by neutralisation with barium carbonate and extraction of the residue with absolute alcohol) and evaporated under diminished pressure. The dry residue was extracted thrice with 25 c.c. of hot alcohol. These extracts, on removal of the solvent under diminished pressure, left a dry residue, which was heated during 15 minutes on the water-bath with 6 g. of sodium acetate and 30 c.c. of acetic anhydride. The mixture was poured into ice-water and the β-tetra-acetyl *l*-xylose (2 g.), which crystallised after a few minutes, was filtered off. Extraction of the aqueous solution with ether gave a further 0·6 g. of less pure material. After recrystallisation from dilute alcohol the β-tetra-acetyl *l*-xylose had m. p. 127—128·5° (corr.), $[\alpha]_D^{15}$ + 25·7° (*c* = 3·6 in chloroform). Vargha (*loc. cit.*) gives m. p. 126° and $[\alpha]_D^{20}$ + 25·7°.

l-*Xylosazone.*—4 G. of diethylidene sorbitol were treated as described above. The residue from the alcoholic solution was heated during 2¼ hours on the water-bath with 45 c.c. of water, 8 g. of phenylhydrazine hydrochloride, and 5 g. of sodium acetate. The yield of pure *l*-xylos-azone, m. p. 159—161°, was 2·4 g.

93. *The Transformation of* d-*Catechin into Cyanidin Chloride.*

By HERBERT APPEL and ROBERT ROBINSON.

IN Freudenberg's experiments leading to the full elucidation of the relations existing between the isomeric catechins, no single observation was more significant than the formation of *dl*-epicatechin (I) by the catalytic hydrogenation of cyanidin chloride (II) (Freudenberg, Fikentscher, Harder, and Schmidt, *Annalen,* 1925, **444**, 135). Nevertheless the reaction is difficult to bring to a successful conclusion, owing partly to the nature of the product and partly to the necessity for close attention to the activity of the catalyst and other conditions. It occurred to us that the converse transformation of catechin into anthocyanidin, if feasible, would have considerable advantages in that a method would be
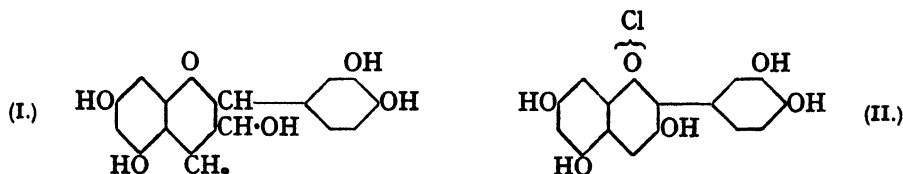
provided for the rapid preliminary study of various naturally occurring catechins, which could be related to anthocyanidins of known and characteristic properties. This could

be carried out even though the specimens were mixtures of stereoisomerides and the results with crude materials would be more decisive than those obtained by alkali fusion.

Such a conversion of catechin into cyanidin has not hitherto been realised, although several investigations on record deal with the formation of other oxonium salts from derivatives of catechin by dehydration and oxidation.

In exploratory work we found that *d*-catechin is a source of a series of coloured products when oxidised by various agents; these were usually unlike cyanidin in properties, being bluish-mauve or orange-red in acid aqueous solution. For example, the action of hydrogen peroxide on a hot alkaline solution of catechin, followed by acidification, furnishes a small yield of an orange oxonium salt, and the oxidation of tetramethylcatechin by means of chloranil in acetic acid solution gives the much bluer type of product.

The first indication of success in the anticipated direction was obtained by the use of brominated ethyl acetoacetate, but bromine in dioxan solution proved to be the key to the solution of the problem.

Judging from the colour changes, the method can be applied to *d*-catechin itself, but a smoother reaction ensues when the tetramethyl ether (III) is employed. Penta-acetyl-catechin does not undergo a similar reaction.
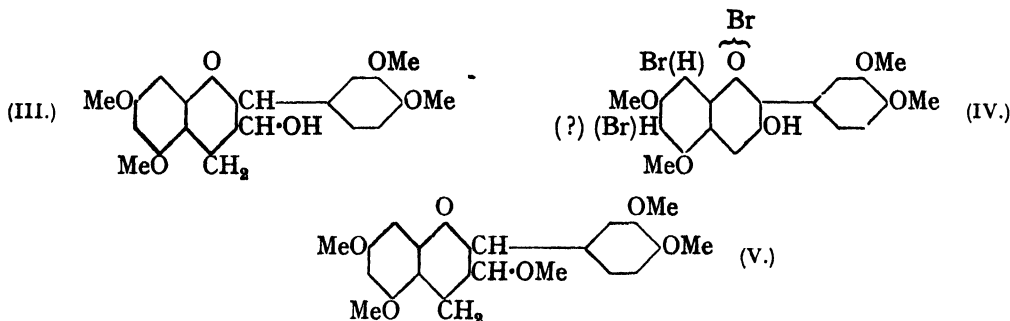
The product of the action of bromine on either the tetramethyl ether or the penta-methyl ether (V) in hot technical dioxan solution is a *bromocyanidin tetramethyl ether bromide* (IV). The demethylation of (V) is strong evidence in favour of the view that the bromine first attacks the secondary alcoholic group.

In regard to the constitution of (IV) we have taken into consideration the fact that Kostanecki and Lampe (*Ber.*, 1906, **39**, 4011) proved that bromocatechin tetramethyl ether is unsubstituted in the pyrocatechol nucleus; the most probable formulation is perhaps as an 8-bromocyanidin tetramethyl ether.

Contrary to previous experience in somewhat analogous cases (compare Willstätter and Robinson, *Ber.*, 1928, **61**, 2505), the demethylation of (IV) by means of hot hydriodic acid and phenol was accomplished satisfactorily; it was accompanied by debromination and the product was cyanidin iodide, convertible into cyanidin chloride of exceptional purity.

It is uncertain whether the addition of phosphorus, not previously employed, is responsible for this improved result or whether it is due to the presence of the bromine atom in the ring.

The cyanidin chloride thus obtained was carefully compared with specimens derived from cyanin (from blue cornflowers) and from synthetic benzoylcyanidin, with the result that no divergences of behaviour could be detected. The outcome is a further proof of the correctness of Freudenberg's catechin formula. If the alcoholic hydroxyl were situated at position 4, it is probable that the product would be a flavone or halogenated flavanone and not a benzopyrylium salt. It may be pointed out, however, that this new process is not of theoretical interest alone, for it also constitutes the most ready method of preparation of cyanidin chloride, especially on a relatively small scale.

Dioxan, recovered and distilled over sodium, could not be utilised for the reaction; this is considered to be due to the removal of the peroxides present in commercial dioxan. These peroxides evidently play an important rôle in the attack on the pyran ring and the question

of the detailed mechanism of this collaboration with the bromine is a very interesting one (compare Hannon and Kenner, J., 1934, 138). Activity is only partly restored to pure dioxan by the addition of benzoyl peroxide; thus, with "good" technical dioxan the yield averages 50%, with pure dioxan a coloration only is produced, and pure dioxan and benzoyl peroxide under the usual conditions afford about 10% of the theoretical yield. We hope to apply this procedure to the tea catechin II or gallocatechin of Tsujimura (*Sci. Papers, Inst. Phys. Chem. Research, Tokyo*, 1934, **24**, 149) and thus to confirm the conclusions of the Japanese chemist by the formation and characterisation of delphinidin.

EXPERIMENTAL.

Bromocyanidin Tetramethyl Ether Bromide (IV).—(A) A solution of bromine (1·85 g., 8 atoms) in technical dioxan (20 c.c.) was added to one of *d*-catechin tetramethyl ether (IV) (1·0 g., 1 mol.; m. p. 142—144°) in dioxan (100 c.c.) at 90°; a deep reddish-violet coloration developed rapidly. After about 20 seconds the mixture was quickly cooled, and crystallisation of the oxonium bromide was facilitated by alternate freezing and fusion of the, solvent. The brownish reddish black crystals possessing a weak green glance were collected (0·8 g.) and washed with dioxan and ether (Found in material dried over phosphoric oxide and potassium hydroxide : C, 44·8; H, 4·3; Br, 29·1; MeO, 23·5. $C_{19}H_{18}O_6Br_2,0·5H_2O$ requires C, 44·6; H, 3·8; Br, 31·3; 4MeO, 24·3%). The *bromide* could not be satisfactorily recrystallised, but the analyses of the crude product (which suggest the replacement of a small proportion of HBr by H_2O) are a sufficient indication of the composition.

The salt dissolves in 0·2% hydrochloric acid to a deep reddish-brown solution and the addition of sodium acetate or carbonate produces a nearly colourless, opalescent precipitate of the pseudo-base. Sodium hydroxide, especially on heating, produces a bright yellow solution when added to the salt or pseudo-base in aqueous or alcoholic media. The alcoholic solution of the salt has the intense bluish-red colour typical of cyanidin and on the addition of much water the pseudo-base is produced. The salt is not extracted from 0·2% hydrochloric acid solution by means of mixtures of toluene and *cyclo*hexanol, but the organic layer contains the pseudo-base.

(B) Under the above conditions, but using dioxan distilled over sodium (b. p. 100—101°), the salt was not isolated. Under the same conditions (pure dioxan) with the addition of benzoyl peroxide (2·0 g.), the yield of the bromide was 0·15 g.

(C) Under the conditions described under (A), but using *d*-catechin pentamethyl ether (V) (1·0 g. containing 7% of crystal-solvent) (Found in material dried in a high vacuum at 56° : MeO, 42·2. Calc. for 5MeO, 43·1%), the yield of bromide amounted to 0·55 g. (Found in material dried over phosphoric oxide and potassium hydroxide : C, 46·3; H, 4·1; Br, 33·3; MeO, 23·8. $C_{19}H_{18}O_6Br_2$ requires C, 45·4; H, 3·6; Br, 31·9; 4MeO, 24·7%). The reactions of this product are the same as those of the salt obtained from the tetramethyl ether. Neither specimen is quite homogeneous, so the question of identity does not arise. The main point, however, is that the salt under discussion contains no phenolic hydroxyl (as shown by the colour reactions) and, as it is a tetramethyl ether, the methoxyl in position 3 of the starting material has been eliminated.

Cyanidin Chloride (II).—A mixture of the crude bromocyanidin tetramethyl ether bromide (1 g.), red phosphorus (1 g.), phenol (6 g.) and hydriodic acid (50 c.c., *d* 1·7) was gently boiled in an atmosphere of carbon dioxide for 2 hours. After cooling, alcohol (10 c.c.), water (90 c.c.), ether (50 c.c.), and light petroleum (50 c.c.) were added and the solution was filtered from phosphorus. The aqueous layer was separated and concentrated under diminished pressure to about 80 c.c.; thereupon cyanidin iodide separated in its characteristic form (yield, 0·25 g.). The iodide was converted into the chloride by means of precipitated silver chloride in an alcoholic solution containing a few drops of concentrated hydrochloric acid. On evaporation of the filtrate on the steam-bath the cyanidin chloride separated in well-formed, straight, chocolate-coloured needles (Found in material dried over phosphoric oxide and potassium hydroxide : C, 53·0; H, 3·9; Cl, 10·8. Calc. for $C_{15}H_{11}O_6Cl,H_2O$: C, 52·9; H, 3·9; Cl, 10·4%). By using the bromide (1 g.) derived from catechin pentamethyl ether, cyanidin iodide (0·15 g.) was isolated and later converted into cyanidin chloride having the usual properties. The cyanidin chloride (*a*) prepared from catechin tetramethyl ether was carefully compared with a specimen (*b*) obtained by the hydrolysis of cyanin chloride and also with a synthetic specimen (*c*). The colours of acid, aqueous, and alcoholic solutions were identical and the known reactions with

sodium acetate, sodium carbonate, sodium hydroxide,* ferric chloride (both colour reaction and rate of oxidative destruction of pigment), and with buffered solutions of graded p_H (conditions of Robertson and Robinson, *Biochem. J.*, 1929, **23**, 35) were observed in all three cases with the same results. Specimen (a) was light chocolate-brown in colour, (b) was much darker brown, and (c) had an intermediate colour, being more like (a) than (b); nevertheless the violet smears on paper were identical and on recrystallisation from aqueous alcoholic hydrochloric acid, by boiling off the alcohol from a test-tube, all three specimens gave prismatic needles having the same appearance under the microscope.

Advantage was taken of the opportunity to make more precise the use of the "cyanidin reagent" introduced by Robinson and Robinson (*Biochem. J.*, 1931, **25**, 1693). This is a mixture of *cyclo*hexanol (1 vol.) and toluene (5 vols.) and we have also used mixtures of *cyclo*hexanol (1 vol.) with toluene (3, 4, 6, and 7 vols.) which may be designated CT3, CT4, etc., according to the number of vols. of toluene.

The comparison was carried out as follows. Specimens (a), (b), and (c) (25·00, 25·04, and 25·03 mg. respectively) were treated in the same way; each was dissolved in 0·5% hydrochloric acid (300 c.c.) (cold solutions were deeper, browner, and bluer-red than the hot solutions), and 25 c.c. of this solution, mixed with an equal volume of 0·5% hydrochloric acid, were shaken with 50 c.c. of CT3; the experiment was repeated with CT4, CT5, CT6, and CT7. The organic layers were separated and formed a graded series of diminishing tinctorial intensity. The CT7 solutions from (a), (b), and (c) were directly compared in the colorimeter and found to be identical; the same was true for the CT6 solutions; and the CT5, CT4, and CT3 solutions gave the same information, but were diluted with an equal, double, and treble volume of 0·1% alcoholic hydrogen chloride, respectively, before colorimetric examination.

Under the above conditions the ratios of pigment concentration in the organic layers were found to be : CT7/6/5/4/3 = 1/1·74/3·32/5·18/9·95. Only adjacent members of the series were directly compared.

Determinations of the distribution number were made with CT3, CT4, and CT5. 10 C.c. of the organic layer with 10 c.c. of 0·5% hydrochloric acid were made up to 60 c.c. with 0·1% alcoholic hydrogen chloride. This solution was compared with 10 c.c. of the aqueous layer along with 10 c.c. of CT similarly made up to 60 c.c. The results were : CT3, D.N. 59·6 (b), 58·4 (c); CT4, 30·1 (a), 30·5 (b); CT5, 19·5 (a), 19·9 (c). We are unable to avoid errors of this order in a colorimetric method and the direct comparison described above is much more reliable than the absolute determination of the distribution number. The figures show, however, the striking effect of *cyclo*hexanol in these distribution experiments. It should be added that the compositions of the CT solvent mixtures giving similar ranges for the various anthocyanidins are widely divergent.

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94. *The Synthesis of Compounds related to the Sterols, Bile Acids, and Œstrus-producing Hormones. Part V. The Synthesis of Conjugated Arylhexadienes, and their Behaviour in the Diels–Alder Reaction.*

By A. Cohen.

The "diene-synthesis" introduced by Diels and Alder (*Annalen*, 1928, **460**, 98) has been extended to compounds related to ζ-*phenyl*-Δ^{αγ}-*hexadiene* (III; R = X = H) with the object of studying the cyclisation of the adducts such as 3-β-phenylethyl-1 : 2 : 3 : 6-tetrahydrophthalic anhydride (IV; R = X = H), which would be expected to lead to derivatives of *as*-octahydrophenanthrene (V) as in the analogous cyclisation of 1-β-phenyl-ethyl-Δ^1-*cyclo*hexene (Cook and Hewett, *J.*, 1933, 1099).

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* The initial pure blue colorations produced on the addition of a large volume of 10% aqueous sodium hydroxide to dilute alcoholic solutions of (a), (b), and (c) were identical, but (b) underwent oxidation more rapidly than (a) and (c), which were identical in behaviour. This is shown by a colour change to green and ultimately brownish-yellow. This "oxidation test" is remarkably sensitive towards the presence of catalysts, and the specimen (b) doubtless contains a trace of a foreign substance which accelerates the reaction. Delphinidin is one of the compounds which are known to produce such an effect.

By such reactions, and employing the different addenda which are known to undergo the Diels–Alder reaction, it was sought to obtain suitable derivatives of (V) which would serve as intermediates in the synthesis of compounds structurally related to œstrone. For this hormone, the constitution (VI) has now been completely established by synthetical reactions (Cohen, Cook, Hewett, and Girard, J., 1934, 653; Cohen, Cook, and Hewett, this vol., p. 445). Moreover, compounds of type (V; X = OMe) would probably have marked œstrogenic activity, for this structure is closely related to those almost certainly possessed by certain lactonic and acidic degradation products of œstriol monomethyl ether, obtained by MacCorquodale, Levin, Thayer, and Doisy (*J. Biol. Chem.*, 1933, **101**, 753) by oxidative fission of the five-membered ring, and stated by them to have several times the œstrogenic activity of œstrone.

A number of dienes of type (III) were prepared, but the reactions of these compounds with maleic anhydride did not proceed normally. Only from ζ-phenyl-Δ$^{α\gamma}$-hexadiene itself was a crystalline *adduct* (IV; R = X = H) obtained in 20% yield.

The arylhexadienes (III; X = H, R = Me; X = OMe, R = Me; X = OMe, R = H), which failed to react normally, yielded resinous products in addition to varying amounts of unchanged maleic anhydride. These products contained amorphous alkali-soluble fractions, the physical properties of which were consistent with polymeric addition products. Such results have already been recorded for certain alkyl butadienes by Farmer and Warren (J., 1931, 3223), who have drawn attention to the polymerising influence of maleic anhydride on conjugated dienes. Further it is probable that the reagent also induces non-additive polymerisation of the diene through an intermediate derivative of vinyltetralin, for it is known that such cyclisation can be effected by reagents which normally induce polymerisation of olefins.
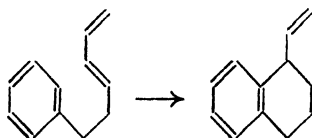

The phenylethyltetrahydrophthalic anhydride (IV; R = X = H) was unexpectedly resistant to the action of cyclising reagents, and under none of the conditions described in the experimental section was there any evidence of the formation of the octahydrophenanthrene derivative (V; R = X = H). In an experiment in which the anhydride was not directly recovered unchanged, it was heated with sulphuric acid in acetic acid at 100° and was converted into a resinous substance. The latter yielded, however, on dehydrogenation with selenium, 3-β-*phenylethylphthalic anhydride* as the only crystalline product, and not the desired anhydride of phenanthrene-1 : 2-dicarboxylic acid. Cyclisation was in no way facilitated by opening the anhydride ring. The *methyl hydrogen* ester corresponding to the anhydride (IV; R = X = H) was submitted to the action of sulphuric acid, to which reference was recently made by Darzens (*Compt. rend.*, 1934, **199**, 1426) for the cyclisation of somewhat analogous arylated unsaturated acids to hydronaphthalene derivatives. The product, in the present instance, again gave 3-β-phenylethylphthalic anhydride on hydrolysis of surviving ester groups, followed by dehydrogenation. Finally the *dimethyl* ester was shown to be unchanged after prolonged treatment with aluminium chloride, by its conversion at the end of the experiment into the original anhydride.

No explanation can be offered for the persistent failure of these cyclisation attempts, although it may be noted here that 1-phenylacetyl-Δ^1-*cyclo*hexene shows a similar resistance to cyclisation (Cook and Hewett, *loc. cit.*).

The hypothesis that a *p*-methoxyl group would facilitate cyclisation and overcome this resistance could not be tested, as the desired 3-β-3'-methoxyphenylethyl-1 : 2 : 3 : 6-tetrahydrophthalic anhydride (IV; R = H, X = OMe) could not be prepared. The failure to obtain this adduct from maleic anhydride and ζ-m-*methoxyphenyl*-Δ$^{α\gamma}$-*hexadiene* (III; R = H, X = OMe) is consistent with the view enunciated above regarding the polymerising influence of maleic anhydride on the diene, for the cyclisation to a tetralin derivative would be enhanced by the powerful para-activating effect of the methoxyl group.

The first method used for the synthesis of phenylhexadienes (III) consisted in dehydration of the *carbinols* (II; R = H or Me, X = H or OMe) resulting from the action of allyl bromide and magnesium on β-phenylpropaldehyde (I; R = X = H), benzylacetone (I; R = Me, X = H), and m-*methoxybenzylacetone* (I; R = Me, X = OMe). The latter ketone was readily obtained by reduction of *m*-methoxybenzylideneacetone.
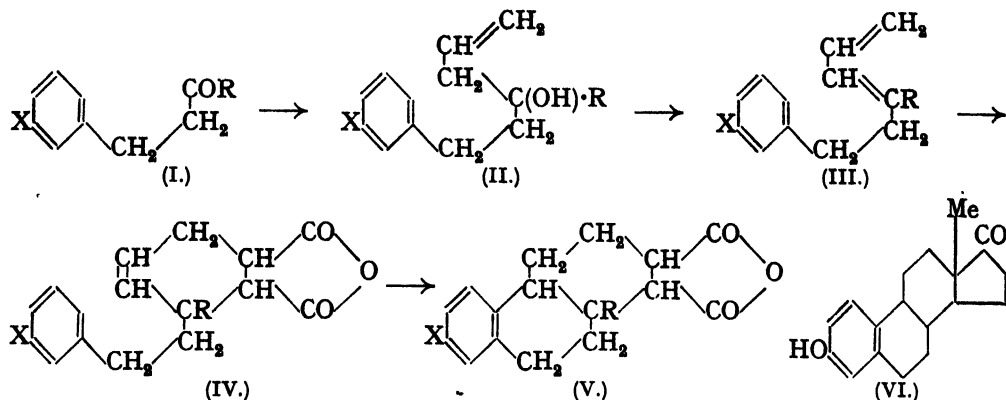

Although carbinols of type (II) could conceivably be dehydrated either to a conjugated, Δ^αγ-, or to a non-conjugated hexadiene, it was anticipated, in view of the well-known tendency of ethylenic linkings to become conjugated (see, for example, Prévost, Donzelot, and Balla, *Compt. rend.*, 1934, **198**, 1041), that the main product would be the desired conjugated diene.

Dehydration of the carbinols (II) was not readily accomplished. Much of ζ-*phenyl-Δ^α-hexen-δ-ol* (II; R = X = H) was recovered unchanged after heating with potassium hydrogen sulphate, the remainder being converted into polymeric material. With the tertiary carbinols (II; R = Me, X = H or OMe) dehydration occurred more readily, but the yields of diene were unsatisfactory on account of its extensive polymerisation to non-volatile substances. The dienes obtained were treated with maleic anhydride (see p. 433), but no crystalline additive compounds resulted.

On account of the poor yields of diene and the uncertainty as to their homogeneity, another route to these compounds was investigated. γ-Phenylpropyl alcohol, readily obtained from benzylmagnesium chloride and ethylene oxide, was converted into its chloride (VII; X = H) by the action of thionyl chloride in the presence of pyridine or dimethylaniline.

γ-Phenylpropylmagnesium chloride was condensed with acraldehyde to give ζ-*phenyl-Δ^α-hexen-γ-ol* (VIII; X = H), which was dehydrated by dropping it on potassium hydrogen sulphate at 150—160° at such a reduced pressure that the diene was removed from the reaction flask as it was formed.
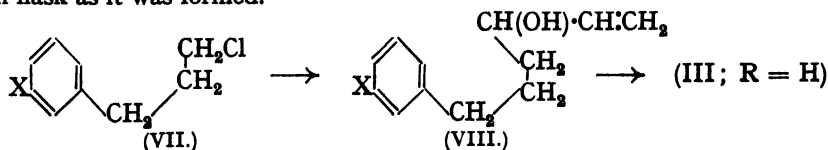
Apart from the very unlikely alternative production of an allene derivative (compare Klages and Klenk, *Ber.*, 1906, **39**, 2552; Reif, *ibid.*, 1908, **41**, 2740), such a reaction could yield only the desired conjugated diene. The product consisted essentially of (III; R = X = H), but contained a small proportion of unchanged carbinol which could not be removed by fractional distillation.

ζ-m-*Methoxyphenyl-Δ^αγ-hexadiene* (III; R = H, X = OMe) was likewise obtained by dehydration of the *carbinol* (VIII; R = H, X = OMe) resulting from the condensation of the magnesium derivative of γ-m-*methoxyphenylpropyl chloride* (VII; X = OMe) with

high-boiling polymeric material, giving a yield of only 10—15% of diene and some unchanged carbinol, but under the following conditions about 50% of crude diene was obtained. The carbinol (28·5 g.) was slowly run through a tapering tap-funnel on finely powdered, freshly fused potassium hydrogen sulphate (43 g.) in a Claisen flask, fitted with a well-cooled receiver, and maintained at 12 mm. pressure in an oil-bath at 145—150°. Under these conditions the carbinol did not readily distil out of the reaction flask. Addition occupied 6 hours and an aqueous oily distillate collected in the receiver. This was dissolved in ether, dried, and, after removal of ether, distilled, giving the crude diene (12·6 g.), b. p. 100—105°/12 mm., and a fraction, b. p. 105—125°/12 mm., which probably contained some unchanged carbinol and was discarded. The *diene* was redistilled over sodium, and was obtained as a light, colourless, mobile liquid, b. p. 99·5—100·5°/11 mm., the carbon content of which (1% below the theoretical) indicated the persistence of a small quantity of carbinol. Repeated fractionation gave a product with the same boiling point as above, having $n_D^{18°}$ 1·5446, $d_4^{18°}$ 0·9304, whence $[R_L]_D$ 53·7 (calc., 53·08) (Found : C, 90·5; H, 9·1. $C_{12}H_{14}$ requires C, 91·1; H, 8·9%).

3-β-Phenylethyl-1 : 2 : 3 : 6-tetrahydrophthalic anhydride (IV; R = X = H).—The above diene (III; X = R = H) (1·6 g.) and maleic anhydride (1·0 g.) were dissolved in warm xylene (2 c.c.), and the yellow solution kept at room temperature for 4 days. The crystalline product which separated (0·65 g.) was recrystallised from benzene–light petroleum, forming narrow colourless leaflets, m. p. 123—125° (Found : C, 75·1; H, 6·7. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%). In other experiments polymerisation also occurred to an appreciable extent, rendering the isolation of the adduct somewhat troublesome. The latter decomposed alkaline permanganate slowly and its bromine absorption was only 75% of the theoretical value, but Diels and Alder (*Ber.*, 1929, **62**, 557, 2084) have noted the difficulty with which similar adducts are attacked by bromine. The anhydride was also hydrolysed with potassium hydroxide in aqueous alcohol, and the acid isolated in good yield as its *acid potassium salt dihydrate*, which crystallised from water in fine needles (Found : loss at 100°, 10·05. $C_{16}H_{17}O_4K,2H_2O$ requires loss, 10·3%. Found : equiv., for anhydrous material, 315; calc., 312).

Cyclisation experiments. (a) The above adduct (1 g.) was treated with aluminium chloride (1·1 g.) in carbon disulphide at 0° and kept thus for 18 hours. After decomposition with ice and dilute hydrochloric acid, the original material was isolated unchanged from the carbon disulphide (m. p. and mixed m. p.).

(b) The same mixture was boiled for 6 hours with the same negative result.

(c) A mixture of the adduct (1·9 g.) and aluminium chloride (2·1 g.) in pyridine (20 c.c.) was kept at room temperature for 4 days. After decomposition as above, and extraction with chloroform, 1·2 g. of unchanged material, m. p. 124°, were obtained as the only crystalline substance.

(d) A solution of the adduct (0·5 g.) in glacial acetic acid (2·5 c.c.) and concentrated sulphuric acid (0·4 c.c.) was heated at 100° for 1¼ hours, cooled, decomposed with ice-water, and extracted with chloroform. The dried extract was evaporated, leaving a viscous oil (200 mg.) which could not be purified. This was heated with selenium (0·3 g.) at 310—320° for 22 hours. The crystalline product, 3-β-phenylethylphthalic anhydride, was sublimed in a vacuum and recrystallised from benzene–light petroleum, forming almost colourless, pointed blades, m. p. 153—154° (15 mg.), identical with the product described below (e).

(e) The adduct was converted by methyl alcohol into its *methyl hydrogen* ester, which crystallised from aqueous methyl alcohol in colourless, lustrous, flat needles, m. p. 137—138° [Found : C, 70·6; H, 7·0 (microanalysis by Dr. A. Schoeller); equiv., 294·5. $C_{17}H_{20}O_4$ requires C, 70·8; H, 7·15%; equiv., 288]. A solution of this (0·3 g.) in 85% sulphuric acid (1 g.) was kept at 12° for 3 days. The acidic product precipitated by water was extracted with chloroform, from which it was removed with sodium carbonate solution. The latter was acidified and extracted with ether. After removal of ether, the residue was freed from ester groups by hydrolysis with 10% aqueous potassium hydroxide (15 c.c.). The resultant acidic product (0·2 g.) was resinous, and was dehydrogenated by heating with platinum-black (50 mg.) at 300° for 6 hours. The crystalline product was dissolved in benzene, filtered, freed from solvent, sublimed at 170°/0·1 mm., and finally recrystallised from *cyclo*hexane, from which *3-β-phenylethylphthalic anhydride* separated in cream-coloured pointed leaflets (30 mg.), m. p. 153—154° (soft at 148°) [Found : C, 76·1; H, 4·7 (microanalysis by Dr. A. Schoeller). $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%).

(f) The anhydride (IV; R = X = H) was converted by methyl-alcoholic hydrogen chloride into the dimethyl ester, a somewhat viscous liquid, b. p. 155—160°/0·1 mm. A solution of the latter (1·5 g.) in carbon disulphide (10 c.c.) was treated with aluminium chloride (1·5 g.)

and kept at 0—4° for 7 days. It was decomposed with ice and a little hydrochloric acid. The carbon disulphide extract was evaporated to dryness, and the residue hydrolysed with 10% potassium hydroxide in aqueous alcohol (25 c.c.). The acidic product was converted into an anhydride by heating with acetyl chloride and finally distilled in an oil-bath at 200°/0·2—0·3 mm. The product separated from benzene–light petroleum in colourless microscopic crystals (0·5 g.), m. p. 123° alone or mixed with the original anhydride (IV; R = X = H).

Methyl m-*Methoxycinnamate.*—This ester, b. p. 162°/13 mm., was obtained in excellent yield by the action of methyl-alcoholic hydrogen chloride on *m*-methoxycinnamic acid, which was obtained, practically in quantitative yield, by the condensation of *m*-methoxybenzaldehyde with malonic acid under the conditions prescribed by Brand and Horn (*J. pr. Chem.*, 1927, 115, 374). Reduction of the ester (17 g.) by sodium and alcohol by Bouveault's method gave an unsatisfactory yield (3 g.) of the required γ-m-*methoxyphenyl-n-propyl alcohol*, b. p. 155—157°/15 mm. (Found : C, 72·0; H, 8·5. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5%), which was purified through its 3 : 5-*dinitrobenzoate*; this crystallised from methyl alcohol in pale yellow plates, m. p. 69—70° (Found : C, 56·5; H, 5·0. $C_{17}H_{16}O_7N_2$ requires C, 56·6; H, 4·5%). A 60% yield of the same alcohol was obtained by similar reduction of the corresponding saturated methyl or ethyl ester. *m*-Methoxycinnamic acid (55 g.) was dissolved in dilute sodium hydroxide solution (*ca.* 500 c.c.) and kept faintly alkaline to phenolphthalein while 1200 g. of 2·5% sodium amalgam were slowly added. Reaction was completed on a warm water-bath. The aqueous solution was acidified, and β-*m*-methoxyphenylpropionic acid separated as an oil which slowly solidified. After crystallisation from benzene–ligroin, the acid, m. p. *ca.* 40°, was esterified with the appropriate alcoholic hydrogen chloride, affording excellent yields of *methyl*, b. p. 148°/15 mm. (Found : C, 67·7; H, 7·2. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%), and *ethyl* β-m-*methoxyphenylpropionate*, b. p. 156—157°/15 mm. (Found : C, 69·0; H, 7·7. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·8%).

For reduction to the alcohol, the ester, preferably the ethyl ester (100 g.), was dissolved in absolute alcohol (400 c.c.) and treated with nut-size sodium (77·5 g.) during 1—1¼ hours. The mixture was heated for 6 hours at 130°. Alcohol was added to remove excess of sodium, and the residual alcohol was distilled off. The pasty mass was treated with a large volume of water, and the product salted out, extracted with ether, and isolated in the usual way. Yield, 48 g. of γ-*m*-methoxyphenyl-*n*-propyl alcohol, which gave the same dinitrobenzoate as that obtained from the reduction product of the corresponding cinnamic ester above.

γ-m-*Methoxyphenyl-n-propyl Chloride* (III; X = OMe).—The alcohol (45 g.) was treated with thionyl chloride (21 c.c.) in dimethylaniline solution (31 c.c.) in the same way as γ-phenyl-propyl alcohol, giving the *chloride* (46·5 g.), b. p. 137°/15 mm. (Found : Cl, 19·0. $C_{10}H_{13}OCl$ requires Cl, 19·2%).

ζ-m-*Methoxyphenyl-Δ^α-hexen-γ-ol* (VIII; X = OMe).—The preceding chloride (37 g.) was converted into a Grignard reagent (4·9 g. of magnesium and 150 c.c. of ether), which was condensed with acraldehyde (12 g.) as in the preparation of (VIII; X = H). The product (29 g.), b. p. 170—175°/15 mm., was converted into the 3 : 5-*dinitrobenzoate*, colourless needles, m. p. 106—107°, from alcohol (Found : C, 59·9; H, 5·4. $C_{20}H_{20}O_7N_2$ requires C, 60·0; H, 5·0%), and the pure *carbinol*, a colourless viscous oil, b. p. 177°/14 mm., regenerated by hydrolysis (Found : C, 75·3; H, 8·9. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%).

Dehydration. The carbinol (24 g.) was added slowly (5 hours) to powdered, freshly fused potassium hydrogen sulphate (38 g.) contained in a vacuum distillation apparatus, maintained at 15—16 mm. pressure, in an oil-bath at 165—170°. The distillate was dried in ethereal solution and redistilled, giving a mobile liquid (11·1 g.), b. p. 140—150°/17 mm. On account of the boiling point range, this was treated again with 24 g. of dehydrating agent in the same way. The final product was fractionated, giving (i) 7·6 g., b. p. 143—145°/17 mm., and (ii) 7·8 g., b. p. 146—150°/17 mm. Fraction (i) was redistilled over sodium, but the product had only 81·3% of carbon (theoretical, 82·9), which could not be increased by redistillation. It was therefore dissolved in benzene (6·1 g. in 7 c.c.), phenyl *iso*cyanate (1 c.c.) added, and the mixture kept at room temperature for 48 hours. The solution was filtered, benzene removed, and the residue distilled (5·2 g.), and redistilled over sodium, giving the pure *diene* (III; X = OMe, R = H) (3 g.), b. p. 149°/18 mm. (Found : C, 82·5; H, 8·7. $C_{13}H_{16}O$ requires C, 82·9; H, 8·6%). When this was treated with maleic anhydride under the various conditions already described, no normal reaction ensued. Varying amounts of maleic anhydride were recovered unchanged, leaving high-boiling resinous residues. The diene was also heated in a sealed tube at 100° for 6 hours with acraldehyde (2 mols.), but 80% of it was recovered as a liquid, b. p. 140°/14 mm.

**95.** *Fused Carbon Rings. Part IV. Further Investigation of* 0 : 3 : 3-bicyclo*Octanones in Relation to the Strain Theory.*

By J. W. BARRETT and R. P. LINSTEAD.

THE investigation of *cis-* and *trans-*bicyclo*octane* derivatives already described (Linstead and Meade, J., 1934, 935; Cook and Linstead, *ibid.*, p. 946) was incomplete in three respects : (1) owing to preparative difficulties, sufficient material of the *trans-*series could not be accumulated for an examination of the physical properties; (2) no absolute proof of configuration was obtained; (3) the structure of *trans*-β-*bicyclo*octanone was not substantiated by oxidation. The completion of this work is now described.*

*trans-cyclo*Pentane-1 : 2-diacetic acid (III) has been prepared in quantity by an improvement of the process of Linstead and Meade (*loc. cit.*) :
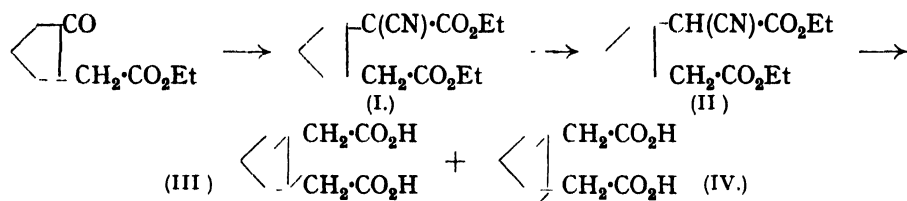
The essential feature is that the mixture of *cis-* and *trans-*acids (IV and III) obtained by the hydrolysis of (II) can be completely freed from the *cis-*isomeride by ketonisation with baryta at 280—300°, and the residual *trans-*acid isolated from the residue in a yield of over 20%.

The melting point of this key-substance was in some doubt. We had previously found values of 132° and 137°, and Hückel and his collaborators obtained preparations melting between 135° and 140°. The purity of this material is essential for the preparation of homogeneous *trans-*bicyclo*octane* derivatives and for resolutions. It is now found that the pure acid melts at 133° and that higher-melting products contain the *cis-*isomeride as impurity. The melting point of the *trans-*acid is raised by admixture with the *cis-*isomeride.

The direct formation of *cis-*β-*bicyclo*octanone in small amount during the hydrolysis of (II) was confirmed. A simple explanation is that preformed dicyclic material is present as impurity in (II), for example, the isomeric imine (V) (compare Best and Thorpe, J., 1909, **95**, 685).
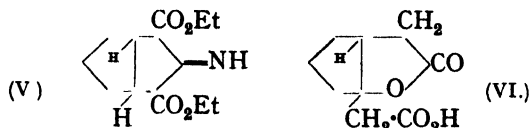
The method by which (V) is formed is obscure. Ring-closure of (II) during the reduction seems unlikely. The alternative explanation is that some unsaturated dicyclic material

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* Since our first publication Hückel, Goth, and Demmler (*Ber.*, 1934, **67**, 2102) and Hückel and Goth (*ibid.*, p. 2104) have described the independent synthesis in small amount of the same intermediate compounds. The methods used were similar to ours and the results are in general agreement. A novel point is that they obtained some *cis-cyclo*pentane-1 : 2-diacetic acid by the oxidation of 5-hydrindanol. This helps to confirm the general stereochemical relationships of these compounds.

is present in (I). Against this is the fact that such a substance would contain a double bond adjacent to the bridge-head and would be strained. Experiments with a view to the isolation of these possible dicyclic intermediates were fruitless.

The preparation of *trans-cyclo*pentane-1 : 2-diacetic acid from the lactone of *cyclo*pentanol-2-acetic acid (Linstead and Meade, *loc. cit.*) was confirmed, but the method is definitely inferior to that mentioned above. This lactone has been more fully investigated by Hückel and Gelmroth (*Annalen*, 1934, **514**, 233). Acid hydrolysis of the unsaturated cyano-ester (I) yielded the *lactonic acid* (VI), but this could not be reduced to a saturated dibasic acid.

cis- and *trans-cyclo*Pentane-1 : 2-diacetic acids are respectively *meso-* and racemic compounds. Hence a resolution of the acid of m. p. 133° would provide absolute evidence of its *trans*-configuration. The acid has been resolved by means of its brucine salt, and a *lævo*-acid, m. p. 151°, $[\alpha]_{5461}^{20}$ — 63·5°, isolated. This and related compounds which are still under investigation will be described in a later paper.

*dl-trans-cyclo*Pentane-1 : 2-diacetic acid gave a 50% yield of *trans-β-bicyclo*octanone when heated with baryta at 340°. Blanc's process gave a poorer yield of the same product. Hückel, Goth, and Demmler (*loc. cit.*) obtained only a trace of ketone by Blanc ring closure of a crude *trans*-acid of melting point 139—140°. In Table I our yields are compared with those obtained from the *cis*-acid under similar conditions.

TABLE I.

Yields, %, of bicycloOctane Derivatives from cycloPentane-1 : 2-diacetic Acids and Esters.

Method.	*cis-*.	*trans-*.
Baryta	72 at 280° (+ 6%) *	50 at 340° (+ 11%)*
Blanc	61 (+1%)	24 (+ nil)
Dieckmann	44	nil

* Figures in parentheses indicate the recovery of uncyclised acid.

The poor yield in such cyclisations, particularly by the Blanc and the Dieckmann reaction, when there is some resistance to the approach of the carboxyl or carbethoxyl groups, has also been noticed among adipic acids derived from sterols by oxidation (compare Wieland and Dane, *Z. physiol. Chem.*, 1932, **210**, 271; Stange, *ibid.*, 1933, **218**, 74; Vocke, *Annalen*, 1933, **508**, 1).

*trans-β-bicyclo*Octanone (regenerated from its carefully purified semicarbazone) was oxidised by both nitric acid and potassium permanganate to *trans-cyclo*pentane-1-carboxy-2-acetic acid in good yield,* the product being identical with synthetic material (Cook and Linstead, *loc. cit.*). The structure of the ketone is therefore established. Reduction of its semicarbazone by the Kishner–Wolff method yielded trans-bicyclo*octane*. Owing to the large amount of *cis-β-bicyclo*octanone obtained as a by-product in the preparation of *trans-cyclo*pentanediacetic acid, it was possible thoroughly to purify this ketone and the derived *cis-bicyclo*octane for determinations of physical constants. The *trans*-ketone was also obtained pure, but *trans-bicyclo*octane has so far been obtained only in small amount.

TABLE II.

Physical Constants of bicycloOctane Derivatives.

	*cis-bicyclo*Octane.	*trans-bicyclo*Octane.	*cis-β-bicyclo*Octanone.	*trans-β-bicyclo*Octanone.
B. p./mm.	136°/755	132°/755	78°/10, 195°/755	62°/10, 189°/755
M. p. (corr.)	(liquid at −70°)	−36°	−33° to −34°	+13° to +14°
$d_4^{18°}$	0·8718	0·8626	1·0102	0·9963
$n_D^{18°}$	1·4629	1·4625	1·4811	1·4791
$[R_L]_D$	34·74	35·12	34·97	35·34
Exaltation	−0·01	+0·37	+0·21	+0·58

* Previous oxidations (Linstead and Meade, *loc. cit.*) had yielded an oil which deposited a trace of solid *cis-cyclo*pentane-1-carboxy-2-acetic acid. A considerable quantity of the pure *trans*-ketone has, however, now been oxidised by each of us to the *trans*-acid. The early anomaly was probably due to the facts that the *cis*-ketone had not been completely eliminated and that the *cis*-acid formed by its oxidation crystallised first owing to its higher melting point and lower solubility.

The *cis*-compounds are higher-boiling and lower-melting than their *trans*-isomerides. A similar difference was observed by Hückel in the case of the isomeric decalins and decalones. The older values for the *cis*-compounds (Cook and Linstead, J., 1934, 950) are in good agreement with those quoted above. The Auwers–Skita rule (*Annalen*, 1919, **420**, 92) is obeyed. The difference in the molecular refractivity between pairs of *cis*- and *trans-bicyclo*isomerides is remarkably constant (the *trans*- always having the higher value), thus : decalins, 0·38; α-decalones, 0·37; β-decalones, 0·32; *bicyclo*octanes, 0·38; β-*bicyclo*octanones, 0·36.

The heats of combustion of the two ketones and of the *cis*-hydrocarbon were kindly carried out by Prof. Dr. W. A. Roth and Dr. G. Becker of Braunschweig, to whom we are greatly indebted.

Heats of Combustion

(weights not corrected to vacuum).

	Cals. per g. at 20° (mean of 4).	Kg.-cals per mol.	
		Constant volume.	Constant pressure.
*cis-bicyclo*Octane........................	10,785±3	1187·4	1189·4
*cis-β-bicyclo*Octanone	8,816±3	1094·1	1095·6
*trans-β-bicyclo*Octanone	8,871±2	1100·9	1102·4

Bearing on the Strain Theory.—These results conclusively establish the fact that two five-membered rings can be linked by *trans*- as well as by *cis*-valencies and justify a fuller theoretical treatment than was made in the introduction to Part I.
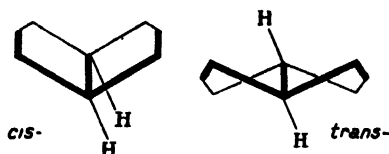
It is generally recognised that the discovery by Ruzicka of stable large carbon rings necessitates the revision of the original Baeyer strain theory. Hückel's investigations of dicyclic ring systems provided strong evidence for the correctness of a purely tetrahedral theory of ring strain (Sachse–Mohr). According to this, rings in which the carbon atoms are tetrahedrally disposed contain the least energy and are stable, and deviations from this state lead to instability. The evidence is not, however, completely explicable on this basis. Both *cis*- and *trans*-forms of the decalin ring may be presumed to contain a tetrahedral disposition of the carbon atoms, yet Hückel has shown that the *cis*-ring is comparatively unstable, for *cis*-α-decalone yields the *trans*-isomeride readily and apparently irreversibly, and Roth and Lassé find that the heats of combustion of *cis*-decalin and *cis*-β-decalone are higher than those of their *trans*-isomerides (*Annalen*, 1925, **441**, 48). Even more unexpected are the results from the hydrindane series, for which the tetrahedral theory requires a strainless *cis*- and a strained *trans*-arrangement.* Here again the heats of combustion give anomalous results (Hückel and Friedrich, *Annalen*, 1927, **451**, 132; Hückel, "Theoretische Grundlagen der Org. Chemie," 1934, p. 63). On the other hand, the available evidence suggests that *cis*-α-hydrindanone is more stable than the *trans*-isomeride (Windaus, Hückel, and Reverey, *Ber.*, 1923, **56**, 95), and experiments in these laboratories by Dr. A. H. Cook point in the same direction but are inconclusive.

These conflicting facts have led to the suggestion that the stability of dicyclic rings—

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* It is necessary to draw attention to two errors in a recent paper by Tudor and Vogel (J., 1934, 1250). After describing the accepted stereochemical arrangement of the *trans*-hydrindane molecule, these authors say " A possible but less probable alternative for the *trans*-system is a planar 5-ring and a planar (and therefore strained) 6-ring (see Hückel, *Fortschr.*, 1927, **19**, Heft 4, 31)." It is self-evident that it is impossible to join any two planar rings by *trans*-valencies and the " alternative " is therefore incorrect. The stereochemistry of the system is correctly discussed by Hückel in the reference cited. Tudor and Vogel conclude from their experiments that " there is some real difference [between the *trans*-decalin and the *trans*-hydrindane system]. . . . This conclusion . . . differs from that of Thorpe (J., 1931, 1023), who regards both ring systems as strainless. A possible interpretation of this difference is that the methods employed [by Thorpe's school] . . . are not sufficiently sensitive to detect the small differences present." The actual conclusion drawn by Thorpe in the reference cited reads as follows : " We are therefore faced with the fact that when the six-membered ring is locked in this way all strain ceases or is so far diminished as to be incapable of detection by the methods we have applied." The " possible interpretation " of Tudor and Vogel has thus already been made and their comment is a misrepresentation.

and hence by implication of simple rings—may be affected to a greater extent than has been previously thought by factors other than strain, in particular the repulsive forces of the constituent atoms (Hückel, *Fortschr. Chem. Physik phys. Chem.*, 1927, **19**, 1; Mills, *Rep. Inst. Solvay*, 1931, 17). If it is admitted that this may be a major factor, we can no longer be sure that the well-known instability of rings containing fewer than 5 carbon atoms is due primarily to their divergence from a tetrahedral arrangement.

The isomeric *bicyclo*octanes yield decisive evidence on this point. The *cis*-form contains two inclined planar *cyclo*pentane rings and is strainless; the *trans*-system contains two multiplanar *cyclo*pentane rings, and there is considerable divergence from the tetra-

hedral arrangement. On the other hand, the interatomic repulsions will be *less* in the *trans*- than in the *cis*-compound. Hence, as Hückel says, "The investigation of this system can bring about a decision of the suitability of the regular tetrahedron. If it were shown that here the *trans*-form was poorer in energy than the *cis*-, the conception of the regular tetrahedron would have to be abandoned" (*op. cit.*, p. 67).

The methods by which the stability of isomeric cyclic compounds can be compared are : (a) From the differences between their heats of combustion. The assumption is made that for practical purposes this is parallel to the difference between their free energies; this is probably justified for compounds of similar physical characteristics. (b) Less rigidly, by measurements of the equilibrium between interconvertible isomerides, and by comparison between the ease of formation and the ease of fission of the two ring systems.

The ease of fission of *cis*- and *trans-bicyclo*octanes has not been compared, but the other methods show that the trans-*system is richer in energy and less stable than the* cis-. Thus, *trans*-α-*bicyclo*octanone is converted into the stable *cis*-isomeride under the conditions of formation (Cook and Linstead, *loc. cit.*); the greater ease of formation of the *cis*-β- over *trans*-β-*bicyclo*octanone is illustrated in Table I; and the difference between the heats of combustion of the isomeric β-*bicyclo*octanones (6·8 kg.-cals.) is exceptionally large, and the *trans*-ketone is at the higher level of energy.

The comparative instability of the trans-bicyclo*octane ring therefore provides a rigid proof of the reality of strain in the sense of a resistance of the tetrahedral carbon atom to distortion.* There seems no evidence from this series alone of the operation of any other factor affecting ring-stability, but when the chemistry of ortho-dicyclic systems is considered as a whole, the possibility has to be admitted that, when the strain is small, the stability of the ring may be affected by minor factors.

If the heat of combustion of *cis-bicyclo*octane (1187·4) is compared with that of *cis*-decalin (1499·9),* the difference for each CH_2 is found to be normal (156·2). The corresponding difference between *cis*-β-decalone and *cis*-β-*bicyclo*octanone is also about normal (155·1 for each CH_2). Hückel has calculated on a tetrahedral basis that the strain in the *trans-bicyclo*octane molecule is nearly equal to that of camphor. The difference between the heat of combustion of camphor and that of *trans*-β-decalone, which is a strain-free isomeride, is 10·6 kg.-cals. (Roth's values). A more direct comparison, because between *two liquids* of similar boiling point, may be made between the isomeric fenchane and *trans*-decalin. The former, which has the same strain as camphor, has a heat of combustion of 1502·1 (Zubov–Swientoslavski); the latter, which is strain-free, a value of 1494·8 (Roth–Hückel). The difference, 7·3 kg.-cals., is very close to that (6·8) now found by Roth and Becker between the isomeric β-*bicyclo*octanones, between which on the tetrahedral theory there should be the same difference in energy.

* This and the other older values are taken from the compilation by Roth in Landolt–Börnstein " Tabellen " (1923, I, 1591; 1927, 331) and represent kg.-cals. per mol. at constant volume.

EXPERIMENTAL.

Preparation of trans-cyclo*Pentane*-1 : 2-*diacetic Acid and of* cis- *and* trans-β-bicyclo*Octan-ones.*—Ethyl *cyclo*pentanone-2-acetate was prepared by Linstead and Meade's method. Light petroleum (b. p. 60—80°) is a more convenient solvent than benzene for the preparation of the intermediate ethyl *cyclo*pentanone-2-carboxylate-2-acetate. With a view to improving the poor yield previously obtained in the condensation of this keto-ester with cyanoacetic ester, the condensation of *cyclo*pentanone and cyanoacetic ester in the presence of piperidine was first systematically investigated; the tabulated figures indicate the yields of solid ethyl *cyclo*pentylidenecyanoacetate obtained from 5 g. of *cyclo*pentanone and 6·8 g. of cyanoacetic ester in the times stated :

Hours at room temp.	¼	1	2	4	—	—	—	—	¼	1	3	4
Hours at 100°	—	—	—	—	¼·	1	2	4	¼	¼	1	¼
Yield, g.*	—	0·1	0·1	0·9	0·6	1·9	2·8	4·7	2·4	2·6	4·3	4·9
Yield, g.†	4·9	5·8	6·2	7·9	6·1	6·8	6·9	7·9	7·0	7·6	7·8	8·0

Catalyst : piperidine, *0·25 g., †1 g.

An increase in the concentration of cyanoacetic ester did not quicken the reaction. The rate of condensation obviously depends upon the concentration of piperidine, and a maximum yield of about 75% is obtainable. An increase in piperidine concentration had a good effect also on the much slower reaction between *cyclo*pentanone-2-acetic ester and cyanoacetic ester. 900 G. of the keto-ester, 600 g. of cyanoacetic ester, and 25 g. of piperidine were left for 14 days in a stoppered bottle. On distillation the mixture yielded 55% of unchanged esters (b. p. 90—125°/12 mm.), which were left to condense with a further quantity of piperidine, and 41% of the condensation product (I). After two distillations the latter boiled completely at 177°/2 mm.—172°/1 mm. and partly solidified. The solid formed clusters of small prisms, m. p. 58°, from light petroleum. The unsolidified portion boiled at 172—174°/2 mm. Both were unsaturated to the usual reagents [Found : (solid) C, 63·6; H, 7·1; (liquid) C, 63·6; H, 7·3. Calc. for (I) : C, 63·4; H, 7·2%]. The liquid presumably contains some isomeride differing in the position of the double bond. The original ester of Linstead and Meade (which was mainly prepared by the use of potassium ethoxide as catalyst) had a wider boiling range, yielded no solid, and was more readily reduced by hydrogen over platinum.

The solid ester (I) was hydrolysed with 3 vols. of boiling hydrochloric acid for 36 hours. The product was evaporated to dryness under reduced pressure, extracted with sodium bicarbonate solution, acidified, and isolated by means of ether. The oil obtained solidified on standing and yielded massive octahedra, m. p. 83°, from benzene–petroleum. A similar hydrolysis of the crude ester (I) gave the same product, which was a saturated lactonic acid and appeared to be the *lactone* of cyclo*pentanol*-1 : 2-*diacetic acid* (VI) (Found : C, 58·5; H, 6·5; acid equiv., 184·4; lactone equiv., 183. $C_9H_{12}O_4$ requires C, 58·7; H, 6·6%; equiv., 184). It gave no definite compound on reduction with zinc and acid, sodium amalgam, or phosphorus and hydriodic acid.

Reduction of (I) (compare Linstead and Meade, *loc. cit.*). Only in a few isolated cases could any catalytic reduction be obtained over Adams's platinum catalyst. Hydrogenation over palladium on barium sulphate or Raney's catalyst also proved abortive. Aluminium amalgam gave consistent yields of 75% on a fairly large scale. The saturated ester (II) boiled at 172°/2 mm. (Found : C, 63·1; H, 7·8. Calc. : C, 62·9; H, 7·9%).

Hydrolysis of (II). 200 G. of the saturated ester were refluxed with 500 c.c. of concentrated hydrochloric acid for 12 hours, and steam-distilled. *cis-bicyclo*Octanone (b. p. 78°/10 mm.; semicarbazone, m. p. 197—198°) was isolated from the distillate in 4% yield in the manner already described (*loc. cit.*). The residue from the steam distillation deposited 110 g. (79%) of mixed *cyclo*pentane-1 : 2-diacetic acids, and ether extraction of the filtrate yielded practically nothing more. The acids melted crude at 149—155° and at 155—156° after one crystallisation from water (Found : equiv., 93·0. Calc., 93·05). Twelve fractional crystallisations from water yielded the pure *cis*-acid, m. p. 172—173°, as the least soluble product; the most soluble fraction melted at 137—138° but was not pure *trans*-acid (see below). Fractional crystallisation of various salts gave no useful separation, although the disodium salt of the *cis*-acid was relatively sparingly soluble in water and gave some pure *cis*-acid.

Separation and Ring Closure of Diacetic Acids.—(1) The separation by the Dieckmann method previously reported was confirmed, but the overall yield was not good. The diethyl ester from 20 g. of mixed acids, m. p. 155—156°, ultimately yielded 4·1 g. of *cis-bicyclo*octanone

(44%) and 0·75 g. (5%) of *trans*-acid, m. p. 132°. The following is the best process for the separation of the *trans*-acid.

(2) A mixture of 60 g. of the acid of m. p. 155—156° with 5 g. of baryta was heated in a bath of mixed nitrates at 280°; the *cis*-ketone distilled regularly. When the evolution of ketone slackened, the temperature was kept at 300° for 2 hours. The black residue was extracted twice with boiling, very dilute hydrochloric acid, which deposited the *trans*-acid, m. p. 131°. After one crystallisation from benzene and one from water, *trans-cyclo*pentane-1 : 2-diacetic acid was obtained pure as massive transparent cubes, which effloresced on exposure to air (Found : C, 58·0; H, 7·6; equiv., 93·0. Calc. : C, 58·0; H, 7·6%; equiv., 93·05). The *cis*-β-*bicyclo*octanone formed during this reaction was isolated by means of a little petrol (b. p. 40—60°) and washed with sodium bicarbonate solution and water. After being dried and freed from solvent, it boiled at 78°/15 mm., and gave a semicarbazone, m. p. 198° after one crystallisation. The bicarbonate extract yielded a small quantity of mixed acids (m. p. 152—154°). Yield : 13 g. (20%) of *trans*-acid and 22 g. (55%) of *cis*-ketone.

The pure *trans*-acid melts sharply at 133°, and no higher-melting acid has been obtained in a number of these cyclisations. When the acid is heated at 280—300° with baryta for some time, it gives no ketone and is recovered almost quantitatively and unchanged in melting point. On the other hand, 11·2 g. of acid of m. p. 137—138° (obtained by exhaustive crystallisation of the mixed acids) on similar treatment gave 7·5 g. of the *trans*-acid (m. p. 132—133°) and 2·1 g. of the semicarbazone of *cis*-β-*bicyclo*octanone (m. p. 197—198°). The material of m. p. 137—138° is thus a mixture of about 70% of *trans*- and 30% of *cis*-acid. Intimate mixtures of the two acids in known quantities melted sharply at the temperatures given below :

% *trans*-Acid	0	10	25	50	66·6	75	80	95	100
M. p.	173°	167·5°	159·5°	147·5°	140°	136·5°	135°	133·5°	133°

(3) When treated with baryta in exactly the same way, the pure *cis*-acid (m. p. 172—173°) gave 72% of *cis*-ketone, and 6% of the *cis*-acid was recovered (compare Linstead and Meade, *loc. cit.*). 10 G. of the *cis*-acid were heated slowly to 230—240° with 25 c.c. of acetic anhydride. When the distillation slackened, the temperature was kept at 260° for 30 minutes. The ketone isolated in 61% yield was the pure *cis*-isomeride (semicarbazone, m. p. 197—198°), and 1% of the *cis*-acid (m. p. 172°) was recovered.

(4) A mixture of 20·2 g. of the *trans*-acid (m. p. 132—133°) and 1·5 g. of baryta was heated by a mixed nitrate bath to 320° (internal temperature) without evolution of ketone. Reaction commenced between 320° and 330°, ketone was evolved freely at 340°, and the process was complete at 350° after 2 hours. *trans*-β-*bicyclo*Octanone, isolated in the usual way, boiled at 61—62°/10 mm. (yield, 50%) and gave the insoluble semicarbazone already described by Linstead and Meade, m. p. 243—245° (crude). 10·1 G. of this were just dissolved by 2·5 l. of boiling methyl alcohol, and the solution deposited 9·9 g. of the pure semicarbazone in massive transparent rhombs, often aggregated in star-like clusters, m. p. 249° (decomp.). The melting point depends upon the rate of heating; the above values were obtained with samples put in a bath at 240°. In spite of the prolonged heating in this cyclisation, as much as 2·25 g. (11%) of *trans*-cyclo*pentanediacetic acid were recovered, m. p. 132—133°.

Purification of the β-*bicyclo*octanones. The yields of pure semicarbazones obtained from the distilled ketones are remarkably high. The *cis*-ketone gives 95·3% of the semicarbazone, m. p. 197—198°, and the *trans*-ketone 98% of that of m. p. 249°. The *cis*-ketone was regenerated in the usual way and was extracted with purified light petroleum. The solution was washed with sodium bicarbonate solution and water and dried over sodium sulphate. The ketone was distilled from a Claisen flask to which a long side-arm carrying a short condenser was fused, so that the vapour did not come into contact with corks (Found : C, 77·3; H, 9·8%). *trans*-β-0 : 3 : 3-bicyclo*Octanone* was regenerated and purified similarly (Found : C, 77·3; H, 9·8. $C_8H_{12}O$ requires C, 77·4; H, 9·8%). For determination of the physical constants (Table II) the ketones were distilled in a vacuum in an all-glass apparatus and the data were determined on small middle fractions, although each ketone distilled constantly.

Oxidation of the trans-*ketone*. (1) The regenerated ketone (0·5 g.) was added during 15 minutes to 4 c.c. of concentrated nitric acid at 90—100° under reflux. The mixture was heated for a further 15 minutes and then left over caustic potash in a vacuum desiccator. The semi-solid mass was shaken with sodium bicarbonate solution and ether. The bicarbonate extract was then acidified and extracted with ether. The residue from the ether was an oil which rapidly solidified in a vacuum desiccator. It was extracted with three successive quantities of 50 c.c. of boiling petroleum (40—60°). Each extract deposited the same product, m. p. 60°, and

there was scarcely any residue undissolved after the third extraction. The material of m. p. 60°, twice crystallised from petroleum (b. p. 40—60°), formed small white needles, m. p. 64°, and 64—65° on addition of the synthetic *trans*-cyclopentane-1-carboxy-2-acetic acid (m. p. 66°) of Cook and Linstead (*loc. cit.*) (Found : C, 55·7; H, 6·9. Calc. : C, 55·8; H, 7·0%).

(2) The regenerated ketone (0·5 g.) in 12 c.c. of acetone was added to 1·28 g. of potassium permanganate dissolved in 60 c.c. of water. The mixture was shaken in a stoppered bottle for 48 hours, the acetone removed in steam, and the solution acidified, cleared with sulphur dioxide, and extracted with ether. The acid in the extract was purified through sodium bicarbonate and by extraction with boiling light petroleum in exactly the same way as was that from the nitric acid oxidation. It melted at 63—64° and did not depress the melting point of the latter product or of the synthetic acid.

cis-bicyclo*Octane*.—A mixture of 18·5 g. of the pure *cis*-semicarbazone (m. p. 197—198°), 17 g. of powdered caustic potash, and a little methyl alcohol (to aid mixing) was heated with a free flame. After removal of the alcohol the *bicyclo*octane distilled at 190—220° (internal temperature). After 2 hours' heating, the distillate was taken up in a little ether, washed with dilute acid, solutions of sodium bisulphite and bicarbonate, and finally with water. After being dried over calcium chloride, the solvent was removed through a short column, and the residue distilled. The fraction (10·6 g.), b. p. 137—139°, from two such runs was refluxed for ¼ hour over sodium and then redistilled twice, the physical properties of the fraction (8·0 g.) of b. p. 137°/755 mm. being taken. It was then distilled over potassium and redistilled (7·6 g.), b. p. 136°/755 mm. The physical properties (Table II) were identical with those observed before the distillation with potassium. For the determination of the heat of combustion a sample was redistilled from an all-glass apparatus and sealed.

trans-bicyclo*Octane*.—3 G. of the *trans*-semicarbazone, m. p. 249°, were evaporated to dryness with 1 g. of sodium and sufficient dry alcohol. The product was heated at 200—220° for ¼ hour, the hydrocarbon which distilled being collected and purified in the manner described above. 0·74 G. of a fraction, b. p. 131—132°/755 mm., was refluxed over sodium for ¼ hour, distilled from sodium, and redistilled; 0·68 g. of 0 : 3 : 3-trans-bicyclo*octane* was isolated, b. p. 132°/755 mm., which was used for the measurement of the physical constants (Table II) (Found : C, 87·5; H, 12·8. C_8H_{14} requires C, 87·2; H, 12·8%).

A solid *by-product*, isolated from the crude hydrocarbon, crystallised from dilute alcohol in long transparent prisms, m. p. 188°. It was soluble in the usual organic solvents, insoluble in water, saturated to permanganate, left no residue on ignition, and contained no nitrogen (Found : C, 78·6; H, 10·1%). Its composition is unknown.

Experiments with the (cis-) *Lactone of* cyclo*Pentanol-2-acetic Acid* (compare Linstead and Meade, *loc. cit.*; Hückel and Gelmroth, *loc. cit.*).—25 G. of Δ¹-cyclopentenylacetic acid were heated with 125 c.c. of 50% sulphuric acid on the steam-bath for 20 minutes, 20 g. of lactone, b. p. 125°/16 mm., being obtained (1). An exactly similar result was obtained when a mixture of Δ¹-cyclopentenylacetic acid and cyclopentylideneacetic acid was used (2). Both samples boiled constantly and had the correct equivalents {Found : (1) C, 66·5; H, 8·0; $[R_L]_D$, 31·62; (2) C, 66·5; H, 8·1; $[R_L]_D$, 31·64. Calc. : C, 66·6; H, 8·0%; $[R_L]_D$, 31·58}.

Each sample was converted into the hydroxy-acid, and the velocity of lactonisation of this determined in the usual manner (J., 1932, 128). The two samples gave identical results (50% lactonisation in 8 minutes, 90% in 60 minutes). The curve obtained by plotting the percentage of lactonisation against time showed no inflexion. The equilibrium between hydroxy-acid and lactone in water was determined separately (Boorman and Linstead, J., 1933, 580) and was at 95·8% of lactone for each sample. The results are those expected for a normal γ-lactone carrying β- and γ-substituents and it is concluded that the lactone is the strain-free *cis*-isomeride.

The lactone was converted into ethyl cyclopentane-1-acetate-2-malonate, which again did not give quite the correct analysis (compare Linstead and Meade, *loc. cit.*). 30 G. of this ester yielded 1·0 g. of *trans*-cyclopentane-1 : 2-diacetic acid on hydrolysis with concentrated hydrochloric acid, together with acetic acid and the original lactone. The acid had m. p. and mixed m. p. 132° (Found : C, 57·9; H, 7·6; equiv., 93·1. Calc. : C, 58·0; H, 7·6%; equiv., 93·05).

96. *Syntheses of Polycyclic Compounds related to the Sterols. Part III.*
9-Methyl- and 3' : 9-Dimethyl-cyclopentenophenanthrene.

By D. J. C. Gamble and G. A. R. Kon.

In a discussion of the constitution of strophanthidin it was suggested by one of us (Kon, *Chem. and Ind.*, 1934, **53**, 593, 956) that the structure (I) provisionally adopted by Jacobs and his collaborators (compare Jacobs and Elderfield, *J. Biol. Chem.*, 1933, **102**, 237; 1934, **107**, 143; Elderfield and Rothen, *ibid.*, 1934, **106**, 71) must be abandoned in favour of a formula such as (II) or (III); these two structures have the same arrangement of substituents in rings I and II but differ in the position of the lactone side-chain and the accompanying tertiary hydroxyl group. The principal reason for the suggested change was that the hydrocarbon (IV) has been obtained by the dehydrogenation both of strophanthidin (Jacobs and Elderfield, *J. Biol. Chem.*, 1934, **107**, 143; Jacobs and Fleck, *ibid.*, 1932, **97**, 57) and of uzarigenin (Tschesche and Knick, *Z. physiol. Chem.*, 1933, **222**, 58).
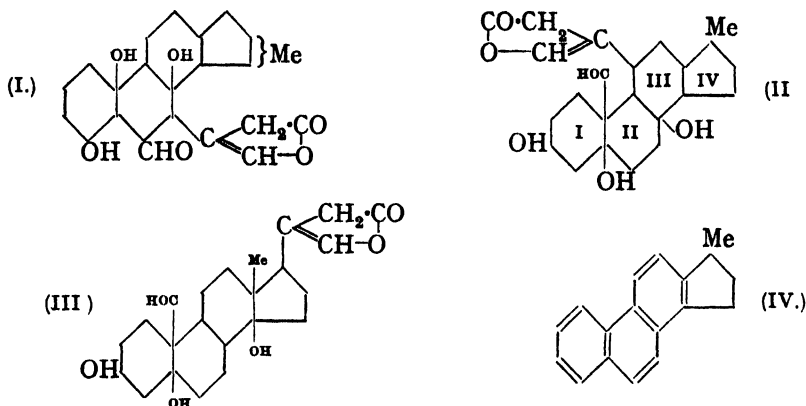
Now it has been proved that uzarigenin has the same carbon skeleton as periplogenin (Tschesche, *Z. physiol. Chem.*, 1933, **222**, 50), which differs from strophanthidin in that the aldehydo-group of the latter is replaced by methyl (Jacobs, Elderfield, Grave, and Wignall, *J. Biol. Chem.*, 1931, **91**, 617); the dehydrogenation of uzarigenin, if the latter had a skeleton such as (I), should therefore lead to a hydrocarbon with a methyl group in the position 9, namely, (V) or (VI):

Although the identity of the hydrocarbon (IV) has been definitely established (Harper, Kon, and F. Ruzicka, J., 1934, 124; Hillemann, *Ber.*, 1935, **68**, 102), its purification is difficult and its identification somewhat uncertain because the melting points of the hydrocarbon and its derivatives are not always depressed by the admixture of closely related compounds. For this reason the compounds (V) and (VI) have been synthesised by the method of Harper, Kon, and Ruzicka (*loc. cit.*). Both are different from (IV), for definite depressions of melting point are observed with mixtures of the hydrocarbons and also of corresponding derivatives. It can therefore be inferred that the skeleton (I) cannot express the structure of strophanthidin and related cardiac aglucones.

The above conclusion had already become probable as a result of the observations of Bernal and Crowfoot (*Chem. and Ind.*, 1934, **53**, 953), which rule out formulæ (I) and (II)

(compare Kon., *ibid.*, p. 956), whilst the correctness of formula (III) was established by Tschesche (*Z. physiol. Chem.*, 1934, **229**, 219) when the present investigation was nearly complete. The formula (III) has also been adopted by Jacobs and Elderfield (private communication from Prof. W. A. Jacobs).

EXPERIMENTAL.

α-(4-*Methyl*-1-*naphthyl*)*ethyl Alcohol*.—28 G. of ethylene oxide in absolute ether were added to an ice-cold solution of a Grignard reagent prepared from 111·5 g. of 1-bromo-4-methylnaphthalene (Meyer and Sieglitz, *Ber.*, 1922, **55**, 1835) and 13 g. of magnesium activated with iodine. The mixture was allowed to reach room temperature and the ether was then distilled off. By the common procedure, 60—65 g. of the *alcohol* were obtained, b. p. 135°/0·5 mm.; it solidified and crystallised from ether–ligroin in lustrous rhombic plates, m. p. 60° (Found : C, 83·7; H, 7·6. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%). The *picrate* formed orange needles, m. p. 107° (Found : C, 55·0; H, 4·3. $C_{19}H_{17}O_8N_3$ requires C, 54·9; H, 4·1%).

The orientation of the bromide employed in the above preparation was checked by its conversion, through the Grignard reagent, into 4-methyl-1-naphthoic acid, m. p. 175—176° (Meyer and Sieglitz, *loc. cit.*), and oxidation of the latter with alkaline permanganate to naphthalene-1 : 4-dicarboxylic acid.

α-(4-*Methyl*-1-*naphthyl*)*ethyl Bromide*.—20 G. of the pure alcohol were heated in a pressure bottle with 100 g. of hydrobromic acid in acetic acid (33% w./v.) for 14 hours at 100°. The *bromide* (23 g.) had b. p. 142°/0·5 mm., solidified at once on cooling, and formed needles, m. p. 45—46°, from ether–ligroin (Found : Br, 32·3. $C_{13}H_{13}Br$ requires Br, 32·1%). The picrate, long orange needles, m. p. 72—73°, was unstable.

1 : 9-*Dimethyl*-1 : 2-*cyclopentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.—50 G. of 2-methyl*cyclo*pentanone were added to a cooled Grignard reagent prepared from the above bromide (93 g.) and 10 g. of activated magnesium, the mixture being then warmed for ½ hour, decomposed with ice and acetic acid, and worked up in the usual way. The desired carbinol (14 g.) distilled at 170—195°/0·2 mm. as a colourless viscous oil with a blue fluorescence; it was accompanied by a fraction, b. p. about 230°/0·4 mm., doubtless αδ-*di*-(4-*methyl*-1-*naphthyl*)*butane*, which formed needles, m. p. 126—127°, from benzene (Found : C, 91·9; H, 7·8. $C_{26}H_{26}$ requires C, 92·3; H, 7·7%), and gave a dipicrate, m. p. 174—175°, and a bis-*s.*-trinitrobenzene compound, m. p. 192—193°. The crude carbinol was dehydrated by heating with 20 g. of phosphoric oxide at 140° for 40 minutes under reduced pressure. The *hydrocarbon* was isolated by addition of ice and extraction with ether, purified by two distillations over sodium, and obtained (7·5 g.) as a colourless viscous oil with a blue fluorescence, b. p. 160°/0·5 mm. (Found : C, 91·3; H, 8·6. $C_{19}H_{22}$ requires C, 91·1; H, 8·9%). A definite picrate was not obtained.

9-*Methyl*-1 : 2-*cyclopentenophenanthrene* (V).—7·5 G. of the above hydrocarbon were heated with 12 g. of selenium for 20 hours at 290—300° (bath temperature). The product, isolated in good yield, was distilled over sodium; after the first few drops of unchanged material had been collected, the distillate solidified and was recrystallised from methyl alcohol, forming long needles, m. p. 109—110°; it was unaltered in m. p. after regeneration from the pure picrate (Found : C, 92·8; H, 7·0. $C_{18}H_{16}$ requires C, 93·1; H, 6·9%). The *picrate* formed orange-red needles, m. p. 153—154°, stable in boiling alcohol (Found : C, 62·2; H, 4·1. $C_{24}H_{19}O_7N_3$ requires C, 62·5; H, 4·2%). The *s.*-trinitrobenzene *compound* formed long yellow needles, m. p. 170—171° (Found : C, 64·5; H, 4·2. $C_{24}H_{19}O_6N_3$ requires C, 64·7; H, 4·3%). The trinitrotoluene *compound* formed pale yellow needles rather soluble in alcohol, m. p. 135—136° (Found : C, 65·2; H, 4·5. $C_{25}H_{21}O_6N_3$ requires C, 65·3; H, 4·6%). The *styphnate* was sufficiently stable to be recrystallised from alcohol and forms yellow needles, m. p. 190—191° (decomp.) (Found : C, 60·3; H, 3·9. $C_{24}H_{19}O_8N_3$ requires C, 60·4; H, 4·0%). The hydrocarbon is more soluble in alcohol than the 3′-methyl isomeride; its derivatives are less soluble and particularly easy to purify.

2 : 5-*Dimethyl*-1-β-(4-*methyl*-1-*naphthyl*)*ethylcyclopentan*-1-*ol*.—The carbinol was prepared exactly as described above, by using 2 : 5-dimethyl- in place of 2-methyl-*cyclo*pentanone. The yield was appreciably improved (23 g. from 60 g. of bromide) by using an excess of magnesium and of ketone, and by distilling off the ether at the end of the operation; the *carbinol* boiled at 185—190°/0·5 mm. (Found : C, 85·8; H, 9·0. $C_{20}H_{24}O$ requires C, 85·1; H, 9·3%). The somewhat high percentage of carbon suggests the presence of some αδ-di-(4-methyl-1-naphthyl)butane. The picrate of the carbinol could not be obtained pure.

1 : 9 : 3′-*Trimethyl*-1 : 2-*cyclopentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.—The dehydration

of the above carbinol gave the *hydrocarbon* in good yield, b. p. 170°/0·6 mm. after redistillation over sodium (Found : C, 90·9; H, 8·9. $C_{20}H_{24}$ requires C, 90·8; H, 9·2%).

9 : 3'-*Dimethyl*-1 : 2-cyclo*pentenophenanthrene* (VI).—16 G. of the above hydrocarbon gave 13 g. of the new *hydrocarbon* on dehydrogenation; this was at first obtained as an oil and was converted into the *picrate*, which crystallised from alcohol–benzene in orange needles, m. p. 134—135° (Found : C, 63·5; H, 4·6. $C_{23}H_{21}O_7N_3$ requires C, 63·1; H, 4·5%). The hydrocarbon regenerated from it formed colourless needles from methyl alcohol, m. p. 80° (Found : C, 92·3; H, 7·3. $C_{18}H_{16}$ requires C, 92·6; H, 7·4%). The s.-trinitrobenzene *compound* formed long yellow needles, m. p. 149—150° (Found : C, 65·2; H, 4·6. $C_{23}H_{21}O_6N_3$ requires C, 65·3; H, 4·6%), the trinitrotoluene *compound* pale yellow needles, m. p. 113—114° (Found : C, 65·9; H, 4·9. $C_{26}H_{23}O_6N_3$ requires C, 65·9; H, 4·9%), and the *styphnate* orange needles, m. p. 159—160°, which tended to decompose somewhat on recrystallisation from alcohol (Found : C, 61·3; H, 4·2. $C_{25}H_{21}O_8N_3$ requires C, 61·1; H, 4·3%).

Styphnate of 3'-*Methyl*cyclo*pentenophenanthrene.*—This derivative, although it cannot be recrystallised, appears to be suitable for the identification of the hydrocarbon owing to its sharp melting point, 135—136°; a specimen prepared from molecular proportions of the components in alcoholic solution formed fine yellow needles (Found : C, 60·0; H, 4·1. $C_{24}H_{19}O_8N_3$ requires C, 60·4; H, 4·0%). The specimen for analysis was prepared from the hydrocarbon obtained by the method of Harper, Kon, and Ruzicka; another specimen, with identical properties, was prepared from the hydrocarbon synthesised by Bergmann and Hillemann's method (*Ber.*, 1933, **66**, 1302). The styphnate of cyclo*pentenophenanthrene*, which was prepared for comparison, melted sharply at 154° and did not depress the m. p. of the foregoing compound; it was not obtained sufficiently pure for analysis.

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97. *The Synthesis of Compounds related to the Sterols, Bile Acids, and Oestrus-producing Hormones. Part VI. Experimental Evidence of the Complete Structure of Oestrin, Equilin, and Equilenin.*

By A. Cohen, J. W. Cook, and C. L. Hewett.

In Part III (Cohen, Cook, Hewett, and Girard, J., 1934, 653) proof was adduced that the ring system of oestrin [*] and equilenin is that of cholesterol, with the hydroxyl group in the same position, independent evidence of the latter feature being also obtained by Haworth and Sheldrick (*ibid.*, p. 864). The present communication deals with the location of the keto-group and the quaternary methyl group of the hormones, and in our view the experiments which we now record not only establish a complete correspondence in molecular structure of the three oestrogenic hormones, oestrone, equilin, and equilenin, but also demonstrate conclusively that the keto-group is at position 17 and the quaternary methyl group at position 13 (sterol system of numbering). Consequently, the only feature of the structure (as distinct from configuration) of these hormones which still remains undetermined is the position of the double bond in equilin (Girard, Sandulesco, Fridenson, Gaudefroy, and Rutgers, *Compt. rend.*, 1932, **194**, 1020). We have not attempted to secure evidence of this, as Dr. Girard has informed us that Professor L. Ruzicka is collaborating with him on this question.

Our results lend strong support to the view that the hormones represent successive stages of dehydrogenation of a sterol molecule, after oxidative removal of its side chain, from which it may be inferred that the animal body contains some factor, possibly an enzyme, capable of inducing dehydrogenation of the sterol ring system. In suitable circumstances such a factor may play an important part in the conversion of one of these

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[*] This term is used to include both oestrone and oestriol, of which the inter-relationship has been established.

natural products into a cancer-producing compound (compare Cook and Haslewood, J., 1934, 428).

With the object of defining the position of the keto-group in oestrone, we submitted its methyl ether to the action of methylmagnesium iodide, then dehydrated the resultant carbinol, afterwards hydrogenated the double bond thus produced, and finally dehydrogenated the ring system by heating with selenium. We expected in this way to obtain a methyl derivative of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene, and clearly the point of attachment of the methyl group would be that occupied by the keto-group of the original hormone.

Now, it was known from previous work (Marrian and Haslewood, *Chem. and Ind.*, 1932, **51**, 277T; Butenandt, Weidlich, and Thompson, *Ber.*, 1933, **66**, 601) that the two alcoholic hydroxyl groups of oestriol, and therefore the keto-group of oestrone, are in the five-membered ring. Consequently, the product of the above series of reactions should have been the 1'-, 2'-, or 3'-methyl derivative of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene. Of these, the 3'-methyl structure was to be preferred, as this would lead to the same position in the molecule for the keto-group of oestrone as that occupied by the side chain of the sterols and bile acids. However, the product from oestrone, which was also obtained in equally good yield from equilin and equilenin, was different from synthetic specimens of all three of these methyl derivatives of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene.

For the synthesis of the 1'- and the 2'-methyl compound we employed an analogous method to that used by Ruzicka, Ehmann, Goldberg, and Hösli (*Helv. Chim. Acta*, 1933, **16**, 833) for the synthesis of 1'- and 2'-methyl-1 : 2-*cyclo*pentenophenanthrene. For the 3'-methyl compound we employed a method analogous to Kon's (Harper, Kon, and Ruzicka, J., 1934, 124) adaptation of the synthetic method used by Cook and Hewett (J., 1933, 1098) for 1 : 2-*cyclo*pentenophenanthrene. The following table, giving the melting points of the synthetic derivatives of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene and their s.-trinitrobenzene complexes, together with those of the analogous compounds prepared from the hormones, shows that these constants are sufficient to characterise the compounds, and to establish their individuality.

	Parent compound.	Synthetic derivatives of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene.			Product from hormones.
		1'-Me.	2'-Me.	3'-Me.	
M. p. of methoxy-compound...	136° (corr.)	98°	137°	148°	166°
M. p. of s.-trinitrobenzene complex	161 ·(corr.)	129	133	137	174

The divergence between the product from the hormones and the three synthetic methyl compounds was apparent from a consideration of the most probable structures of the hormones, for in the carbinols arising from the methyl ethers of the hormones by treatment with methylmagnesium iodide the carbinol group is adjacent to a quaternary carbon atom, provided that the quaternary methyl group is at position 13 and the original keto-group at position 17. But it is well known that dehydration of carbinols of this type is attended by group migration, a somewhat comparable example being found in the dehydration of 2 : 2-dimethyl*cyclo*hexanol, which gives 75% of 1 : 2-dimethyl-Δ^1-*cyclo*hexene and 25% of 1-*iso*propyl-Δ^1-*cyclo*pentene (Meerwein, *Annalen*, 1914, **405**, 129).
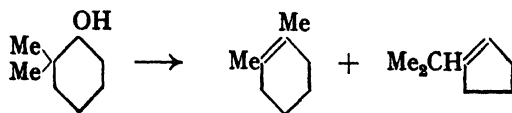
By analogy, dehydration of the carbinols obtained from the hormones involves simultaneous migration of the quaternary methyl group to the adjacent position in the five-membered ring, so that the final product is 7-*methoxy*-3' : 3'-*dimethyl*-1 : 2-cyclo-*pentenophenanthrene* (V), the elementary composition of which is indistinguishable from that of a monomethyl compound. In the series of transformations with equilenin

the pure product was isolated at each stage, and the changes may be formulated as follows:

(I.) Equilenin methyl ether — (II.) — (III.) — (IV.) — (V.)
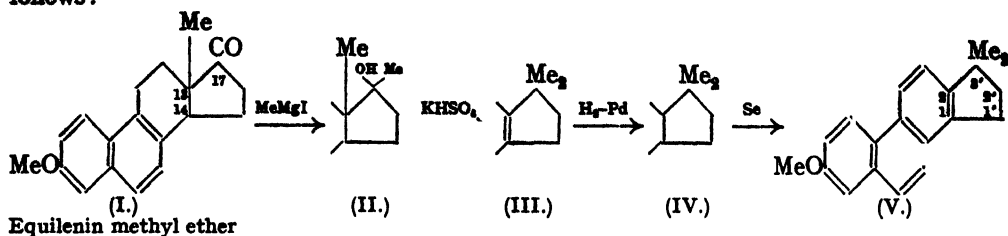
Hydrogenation of the double bond prior to selenium dehydrogenation was effected in order to avoid possible complications due to unsaturation in the five-membered ring. When the reactions with equilin were carried out, the true nature of the changes had been appreciated and it was realised that this previous hydrogenation was superfluous, so the dehydration product of the carbinol was treated directly with selenium. It is significant that the pure, sublimed, and recrystallised product was isolated in 55% yield after heating with selenium at 295—305° for only 7 hours.

Conclusive proof of the correctness of the above interpretation of the hormone transformations was secured by an experiment with the dihydroxyoestratriene which arises by reduction of oestrone (Girard, Sandulesco, and Fridenson, *Compt. rend. Soc. Biol.*, 1933, **112**, 964). The methyl ether of this secondary carbinol would clearly be expected to behave, on dehydration, like the tertiary carbinols already discussed, and this was, in fact, the case. Selenium dehydrogenation of its dehydration product led to 7-*methoxy-3'-methyl*-1 : 2-cyclo*pentenophenanthrene* (VIII), identical with the synthetic sample of this compound :

(VI.) Methyl ether of dihydroxy-oestratriene — (VII.) — (VIII.)
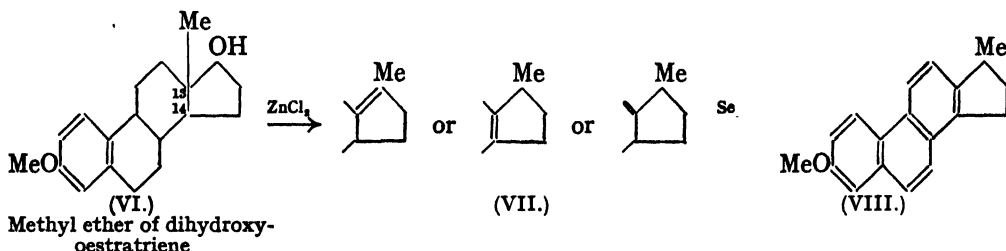
The methyl group which appears at position 3' in the final product is the quaternary methyl group of the original oestrone molecule, and we regard these transformations as supplying indisputable proof of position 13 for this methyl group, for if it were at 14 (the only alternative for equilenin) there would be a free hydrogen atom at position 13, and *normal* dehydration of the carbinol would ensue :

(IX.)
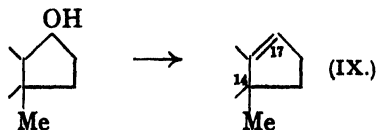
The possibility of migration of methyl from C_{14} to C_{17} during dehydrogenation of a structure such as (IX) is discounted by the experiments with the tertiary carbinols from oestrone and equilenin, when care was taken to hydrogenate the double bond before dehydrogenation of the ring system.

We may recall that it was shown in Part III (*loc. cit.*) that, when the keto-group of oestrone or equilenin was reduced (Kishner–Wolff) to a methylene group and the methyl ether of the product then dehydrogenated, the quaternary methyl group was *eliminated*, leading to 7-methoxy-1 : 2-*cyclo*pentenophenanthrene.

These changes, which thus involve methyl migration by one route to the aromatic

structure, and methyl elimination by another route, find an exact counterpart in some experiments made by Ruzicka and his collaborators (*Helv. Chim. Acta*, 1922, **5**, 581; 1932, **15**, 1300; 1933, **16**, 169) with abietinol, the Bouveault reduction product of the methyl ester of abietic acid. These authors showed that the methyl group migration which accompanied the dehydration of abietinol could be avoided by oxidation to abietinal, followed by Kishner–Wolff reduction of this aldehyde. The hydrocarbon obtained by the first route gave homoretene on dehydrogenation, whereas that obtained by the second method gave retene.
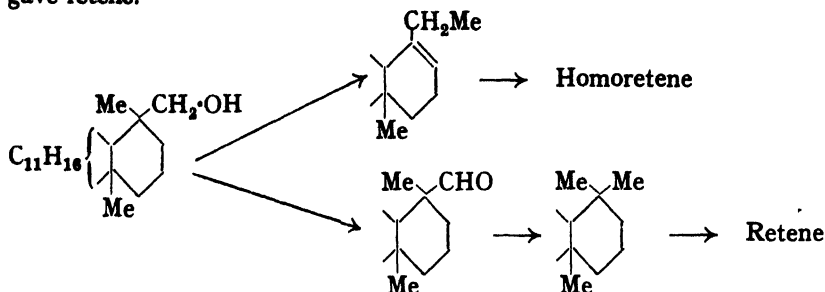
The structure (V) which we assign to the dimethyl derivative of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene receives confirmation by its synthesis by condensation of β-6-methoxy-1-naphthylethylmagnesium bromide with 2 : 2 : 5-trimethyl*cyclo*pentanone, followed by dehydration of the crude carbinol, cyclisation of the product, and then selenium dehydrogenation :
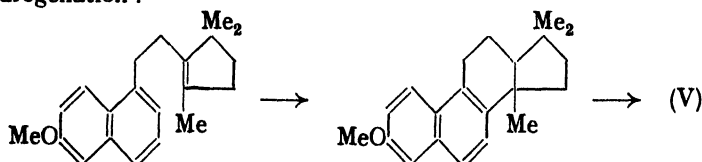
We are indebted to Dr. John Iball for a preliminary X-ray crystallographic examination of 7-methoxy-3' : 3'-dimethyl-1 : 2-*cyclo*pentenophenanthrene from oestrone. X-Ray rotation and oscillation photographs gave the following dimensions of the monoclinic cell :

$$a = 8.75 \text{ Å.}; \quad b = 6.21 \text{ Å.}; \quad c = 28.0 \text{ Å.}; \quad \beta = 90°.$$

The density of the crystal, measured by the flotation method, was 1·188 at 20°. Assuming 4 molecules per unit cell, these values give $274 \pm 1\%$ for the molecular weight, which confirms the theoretical value of 276 for $C_{20}H_{20}O$. The lattice seems to be of the usual layer type with an almost flat molecule, the above cell dimensions being approximately in the directions of the width, thickness, and length, respectively, of the molecules.

DISCUSSION.

The results which we have obtained have a bearing on several problems connected with the sterols and bile acids. For example, the two most important bile acids (cholic and deoxycholic acids) have a hydroxyl group at C_{12}, *i.e.*, the position in ring III adjacent to the quaternary methyl group at C_{13}, and an investigation of the dehydration of certain derivatives of these bile acids is in progress in this laboratory, as it seems likely that methyl migration from C_{13} to C_{12} will be encountered. Moreover, it is now possible to present a rational interpretation of the formation of 3'-methyl-1 : 2-*cyclo*pentenophenanthrene by dehydrogenation of sterols, bile acids, and cardiac aglucones. Clearly the methyl group migration from C_{13} to C_{17} is concomitant with, and inseparable from, the elimination of the side chain, and is in no way dependent on the dehydrogenation. The side chain may be regarded as being expelled from the molecule as an anion ; the whole process then becomes a special case of the transformations which include the pinacolin and Wagner–Meerwein rearrangements (compare Robinson, *Mem. Manchester Phil. Soc.*, 1920, **64**,

No. 4, 1). Support for this view is afforded by the observation of Diels, Gädke, and Körding (*Annalen*, 1927, **459**, 1), which we have confirmed, that 3'-methyl-1 : 2-*cyclo*-pentenophenanthrene ("$C_{18}H_{16}$") is obtained not only by dehydrogenation of cholesterol, or better cholesteryl chloride, but also from the hydrocarbon "$C_{19}H_{18}$" first obtained by Mauthner and Suida (*Monatsh.*, 1896, **17**, 41) by pyrolysis of cholesteryl chloride. In this last process the intact side chain is eliminated, as was clearly shown by the subsequent re-investigation by Fischer and Treibs (*Annalen*, 1926, **446**, 257). We are of the opinion that there are very few examples of group migration which may be ascribed unequivocally to the action of dehydrogenating catalysts, for the well-known migrations which have been observed with various *gem*-dimethyl derivatives of *cyclo*hexane and tetralin have usually occurred under the influence of bromine or nitric acid (compare Baeyer and Villiger, *Ber.*, 1899, **32**, 2429; Crossley, J., 1904, **85**, 264; Crossley and Renouf, J., 1909, **95**, 930; Inhoffen, *Annalen*, 1932, **497**, 134). This undoubtedly involves substitution of, for example, bromine for hydrogen, as an intermediate phase. Elimination of hydrogen bromide from a compound in which bromine occupies an adjacent position to a *gem*-dimethyl group would be just as certainly attended by methyl migration as the dehydration of carbinols of analogous structure. The important point, which we believe is not generally appreciated, is that the migration is not determined *ipso facto* by the dehydrogenation.

The position which we assign on the basis of our present experiments to the quaternary methyl group of the oestrogenic hormones is that which is now fairly generally accepted for one of the quaternary methyl groups in the sterol-bile acid molecule, but as the direct conversion of a sterol into one of the hormones has not yet been achieved we naturally do not claim that our evidence supplies confirmation of this position for the sterol molecule. However, the theoretical considerations underlying the evidence for placing the methyl group at C_{13} in the bile acid molecule (Wieland and Dane, *Z. physiol. Chem.*, 1933, **216**, 91; compare Wieland and Schlichting, *ibid.*, 1924, **134**, 276) have been verified experimentally by the recent work of Cook and Linstead (J., 1934, 946) and we regard the structures of cholesterol and the bile acids as being now completely established in every detail, for if once position C_{13} rather than C_{14} is accepted for one quaternary methyl group the other must be at C_{10} (a position already strongly supported by indirect evidence) to account for the isolation of *n*-butane-$\alpha\gamma\gamma$-tricarboxylic acid from the oxidation products of pyrodeoxybilianic acid (Wieland and Vocke, *Z. physiol. Chem.*, 1928, **177**, 68).

Methods of synthesis of equilenin and allied substances have been explored in this laboratory for some time past, and attention will be concentrated on these investigations now that the constitution of this hormone has been established.

EXPERIMENTAL.

With five exceptions (denoted by asterisks) the analyses were microanalyses by Dr. A. Schoeller.

Experiments with Oestrone.

Oestrone Methyl Ether.—This was obtained from the hormone (2 g.) by heating on the water-bath for 2 hours with methyl *p*-toluenesulphonate (2·6 g.) and 10% aqueous potassium hydroxide (8 c.c.), a second portion (10 c.c.) being added after an hour. The methyl ether was collected, washed, and recrystallised from aqueous alcohol (charcoal). The product (1·7 g.) had m. p. 167·5—169° (compare Butenandt, Störmer, and Westphal, *Z. physiol. Chem.*, 1932, **208**, 167).

Methylcarbinol from Oestrone Methyl Ether.—The finely powdered methoxy-compound (1·5 g.) was gradually added to an ice-cold Grignard solution prepared from methyl iodide (1 c.c.), magnesium turnings (0·4 g.), and anhydrous ether (10 c.c.). After warming to room temperature, the resultant solution was boiled for 2 hours, decomposed with ice and ammonium chloride, and the ether removed by distillation. The crude carbinol was collected (m. p. 95—100°) and used without purification.

Dehydration. The product (1·5 g.) of the Grignard reaction was heated at 160—165° for 1¼ hours with potassium hydrogen sulphate (3 g.). The resinous product was isolated with ether, and distilled at 0·2 mm. from a small flask immersed in an oil-bath at 190—200°. The viscous distillate was obtained crystalline (0·6 g.) from alcohol, and after recrystallisation from alcohol had m. p. 58—60° to a cloudy liquid, clear at 80°. This indefinite m. p. suggested a

mixture of isomerides, for the analytical figures were in good agreement with a structure of type (III) (Found : C, 84·9; H, 9·0. $C_{20}H_{26}O$ requires C, 85·0; H, 9·3%). A higher fraction was obtained from the above distillation by removing the last traces of material in an air-bath. After two recrystallisations from alcohol this (0·1 g.) gave pure oestrone methyl ether (in experiments with the other two hormones the technique was improved and the carbinols obtained from the Grignard reactions were successfully freed from unchanged ketone).

Catalytic Hydrogenation (this operation and also the hydrogenation of the analogous compound in the equilenin series were performed by Mr. G. A. D. Haslewood).—A solution of the aforesaid dehydration product (0·5 g.) in moist ether was shaken for 7 hours with hydrogen and a palladium-black catalyst of proved activity. The resulting colourless gum would not crystallise.

Dehydrogenation. The foregoing gum was heated with selenium (1 g.) at 300—320° for 21½ hours. The crystalline product was extracted with benzene, the solvent removed from the filtered extract, and the residue heated with a little sodium at 180° for a few minutes. The substance was freed from sodium by a second extraction with benzene, and then distilled at 0·15 mm. (air-bath at 140—160°). The distillate was recrystallised from benzene–alcohol (yield, 0·32 g.; m. p. 163—164°) and then twice from alcohol. 7-*Methoxy*-3′ : 3′-*dimethyl*-1 : 2-cyclo*pentenophenanthrene* (V) formed colourless plates (from alcohol) or needles (from benzene), m. p. 166—167°, and had no detectable optical activity (1·4% solution in dioxan) (Found : C, 86·8; H, 7·2; *M*, Rast method, 254, 261. $C_{20}H_{20}O$ requires C, 86·9; H, 7·3%; *M*, 276). This compound, like 7-methoxy-1 : 2-cyclopentenophenanthrene (Part III, *loc. cit.*) and its three synthetic monomethyl derivatives (below), gave a transient carmine colour in concentrated sulphuric acid. The subsequent colour changes were similar with all five compounds, but they differed from one another in the persistence of the intermediate yellow phase and in the final colour (for example, blue-green, olive-green, or murky, but without definite colour).

The s.-*trinitrobenzene* complex of 7-methoxy-3′ : 3′-dimethyl-1 : 2-*cyclo*pentenophenanthrene crystallised from alcohol in golden-orange needles, m. p. 174—175°, and gave a large depression of the m. p. (161°) of the analogous derivative of 7-methoxy-1 : 2-*cyclo*pentenophenanthrene (Found : C, 63·5; H, 4·7. $C_{20}H_{20}O,C_6H_3O_6N_3$ requires C, 63·8; H, 4·7%).

Methyl Ether of Dihydroxyoestratriene (VI).—Sodium (1 g.) was gradually added to a solution of oestrone (1 g.) in boiling ethyl alcohol (50 c.c.). The product was recrystallised from aqueous alcohol and had m. p. 165—168° (lit. 174°) (0·7 g.). This dihydroxyoestratriene, without further purification, was methylated with methyl *p*-toluenesulphonate and 10% potassium hydroxide solution, as described for oestrone. The methyl ether could probably have been obtained in the pure crystalline state, but it was extremely soluble in all media and it was considered expedient to conserve the material for the subsequent operations.

Dehydration and dehydrogenation. · The crude methoxy-carbinol (VI) (0·7 g.) was heated at 170—180° for ¼ hour with powdered anhydrous zinc chloride (1·5 g.) The product, isolated by means of ether, was distilled at 0·05 mm. from an air-bath slowly heated from 115° to 140°. A smaller fraction distilled at 140—160°, and was largely crystalline. After two recrystallisations from alcohol this had m. p. 141—146°, the mixed m. p. with 7-methoxy-3′-methyl-1 : 2-cyclopentenophenanthrene (m. p. 148°) being 143—147°. Thus, partial dehydrogenation had attended the dehydration.

The main distillate (0·5 g.) formed a colourless viscous liquid, and was heated with selenium, (1 g.) at 295—305° for 8½ hours. The crystalline product was extracted with benzene, heated to 170° with a little sodium, and then crystallised from alcohol. The crystals (0·35 g.) were sublimed at 150—160°/0·1 mm., and the sublimate recrystallised from alcohol, yielding 0·2 g. of pure 7-*methoxy*-3′-*methyl*-1 : 2-cyclo*pentenophenanthrene* (VIII), m. p. 146·5—147·5°. · This was crystallised from alcohol with an equal weight of s.-trinitrobenzene. The orange needles, after recrystallisation from alcohol, had m. p. 137—138° and did not depress the m. p. of a synthetic specimen of the s.-*trinitrobenzene* complex of 7-methoxy-3′-methyl-1 : 2-*cyclo*pentenophenanthrene (below) (Found : C, 63·0; H, 4·6. $C_{19}H_{18}O,C_6H_3O_6N_3$ requires C, 63·1; H, 4·5%). The trinitrobenzene was removed from this complex by reduction with stannous chloride in boiling aqueous alcohol. The resulting 7-methoxy-3′-methyl compound (VIII) crystallised from alcohol in colourless leaflets, m. p. 147·5—148·5°, not depressed by admixture with the synthetic specimen (Found : C, 87·1; H, 7·0. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%).

Experiments with Equilenin.

Methylcarbinol from Equilenin Methyl Ether (I).—The finely powdered methyl ether (Part III, *loc. cit.*) (0·75 g.) was gradually added to an ice-cold Grignard solution prepared from methyl

iodide (1 c.c.), magnesium turnings (0·4 g.), and anhydrous ether (10 c.c.). The solution was boiled for 2¼ hours, treated with ice and ammonium chloride, the ethereal solution dried (sodium sulphate), and the ether removed on the water-bath. The residual *carbinol* (II) was recrystallised from *cyclo*hexane, forming tufts of colourless silky needles (0·65 g.), m. p. 133—133·5° (Found : C, 81·3; H, 8·1. $C_{20}H_{24}O_2$ requires C, 81·0; H, 8·2%). The material isolated from the liquors was triturated with a little ether, and the undissolved residue crystallised from alcohol, yielding 30 mg. of unchanged equilenin methyl ether.

Dehydration of the methylcarbinol. This was effected by heating the pure carbinol (0·6 g.) with freshly fused potassium hydrogen sulphate (1·2 g.) at 160—170° for an hour. The *product* (III) crystallised from alcohol (charcoal) in colourless leaflets (0·4 g.), m. p. 131—132° (Found : C, 86·25; H, 7·85. $C_{20}H_{22}O$ requires C, 86·3; H, 8·0%).

Hydrogenation. This was effected in presence of palladium-black and moist ether. After two crystallisations from alcohol the saturated *methoxy*-compound (IV) formed small colourless plates, m. p. 131—132° (Found : C, 85·7; H, 8·55. $C_{20}H_{24}O$ requires C, 85·7; H, 8·6%). There was a large depression of m. p. when this substance was mixed with the original unsaturated compound.

Dehydrogenation. The foregoing hydrogenation product (0·14 g.) was heated with selenium (0·25 g.) at 300—310° for 17 hours. The product was isolated in the usual way, sublimed in a high vacuum, and recrystallised from alcohol, giving 53 mg. of pure 7-methoxy-3' : 3'-dimethyl-1 : 2-*cyclo*pentenophenanthrene (V), m. p. 165—165·5°. The *s.*-trinitrobenzene complex had m. p. 174—175° (Found : C, 63·5; H, 4·7. Calc. : C, 63·8; H, 4·7%). Neither of these m. p.'s was depressed by admixture with the analogous compounds from oestrone.

Experiments with Equilin.

Equilin Methyl Ether.—Methylation of equilin (1 g.) was effected with methyl *p*-toluene-sulphonate and 10% potassium hydroxide solution just as described for oestrone. The *methoxy*-compound (1 g.) crystallised from alcohol (charcoal) in colourless needles, m. p. 160·5—161·5° (Found : C, 80·7; H, 7·8. $C_{19}H_{22}O_2$ requires C, 80·8; H, 7·9%).

Methylcarbinol from Equilin Methyl Ether.—The Grignard condensation with the methoxy-ketone (0·9 g.) was effected as in the equilenin series. The *carbinol* crystallised from benzene-light petroleum in soft colourless needles (0·7 g.), m. p. 133—134° (Found : C, 80·9; H, 8·7. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·8%). Dehydration of the carbinol (0·6 g.) was effected by heating for an hour at 160—170° with potassium hydrogen sulphate (1·2 g.). The product was isolated with ether, distilled in a high vacuum (air-bath at 140—150°), and the distillate crystallised from alcohol. The *product* (0·26 g.) formed colourless needles, m. p. 105—110°, after sintering, this figure being raised to 112—117° by recrystallisation from alcohol (Found : C, 86·2, 86·1; H, 7·7, 7·8. $C_{20}H_{24}O$ requires C, 85·7; H, 8·6%). The heterogeneous nature of this substance was undoubtedly due to the presence of dehydrogenation product, as in the case of the analogous substance from dihydroxyoestratriene. This view was confirmed by the rise in the carbon figure and the fall in the hydrogen figure shown by a fraction, m. p. 132—139°, obtained by two further recrystallisations from alcohol (Found : C, 86·7; H, 7·3%).

Dehydrogenation. The once-recrystallised dehydration product, m. p. 105—110° (0·1 g.), was heated with selenium (0·2 g.) at 295—305° for 7 hours. Pure 7-methoxy-3' : 3'-dimethyl-1 : 2-*cyclo*pentenophenanthrene (V) (55 mg.), m. p. 164—165°, was isolated in the usual way. The *s.*-trinitrobenzene complex had m. p. 174—175° (Found : C, 63·8; H, 4·6. Calc. : C, 63·8; H, 4·7%). The identity of these compounds with the analogous compounds from oestrone was confirmed by mixed m. p. determinations.

Synthesis of 1'- and 2'-Methyl Derivatives of 7-Methoxy-1 : 2-cyclopentenophenanthrene.

Two stages in the synthesis of β-6-methoxy-1-naphthylethyl alcohol (Part III, *loc. cit.*) were improved when the preparation was carried out on a larger scale. (a) When reduction of 1-nitro-6-methoxynaphthalene was effected with aluminium amalgam and aqueous alcohol, the amine was obtained in a satisfactory state of purity without distillation : Boiling water (40 c.c.) was added to a mixture of the nitronerolin (50 g.), amalgamated aluminium strips (55 g.), and absolute alcohol (500 c.c.). After the vigorous reaction had subsided, the whole was heated on the water-bath for 1½ hours, three further quantities of 40 c.c. of water being added during the first ½ hour. The boiling solution was filtered from the alumina sludge, which was well washed with boiling alcohol. The alcohol was removed from the filtrate under reduced pressure, and the residual oil treated with 2N-sulphuric acid (115 c.c.). The resulting

sulphate was collected and recrystallised from water slightly acidified with sulphuric acid. The sulphate was then sufficiently pure for conversion into iodonerolin.

(b) The yield of methoxynaphthylethyl alcohol was improved by adding a molecular proportion of ethyl bromide during the preparation of the Grignard compound of 5-iodonerolin (compare Grignard, *Compt. rend.*, 1934, **198**, 625, 2217). A mixture of iodonerolin (50 g.), ethyl bromide (13 c.c.), and anhydrous ether (350 c.c.) was added, during 1½ hours, to magnesium turnings (8·5 g.), activated with iodine. Boiling was continued for a further 2 hours, and the solution, cooled in a freezing mixture, was slowly treated with ethylene oxide (25 g.) diluted with ether (50 c.c.). After ½ hour, the whole was allowed to warm to room temperature, kept over-night, and the ether then slowly distilled on the water-bath. The product was isolated as previously described. In this way, 85 g. of β-6-methoxy-1-naphthylethyl alcohol were obtained from 170 g. of 5-iodonerolin (yield, 70%).

β-6-Methoxy-1-naphthylethyl Bromide.—Phosphorus tribromide (4·7 g.) was added to a solution of the alcohol (10 g.) in carbon tetrachloride (10 c.c.), previously heated to 60°. After the brisk evolution of hydrogen bromide had ceased, the mixture was kept at 60° for ½ hour, cooled, and well extracted with water and with sodium carbonate solution. The oil was distilled in a vacuum, giving the *bromide* (7·1 g.), b. p. 155°/0·4 mm., as a crystalline distillate, which was recrystallised from alcohol, forming colourless needles, m. p. 57—58° (Found : C, 58·8; H, 5·4. $C_{13}H_{13}OBr$ requires C, 58·9; H, 5·0%). The residue from the distillation was hydrolysed with alcoholic potash, and the product again treated with phosphorus tribromide, giving a further 1·9 g. of the above bromide.

Ethyl 2-(β-6′-Methoxy-1′-naphthylethyl)-5-methylcyclopentanone-2-carboxylate.—The potassio-compound prepared by 3—4 hours' boiling of ethyl 5-methylcyclopentanone-2-carboxylate (Cornubert and Borrel, *Bull. Soc. chim.*, 1930, **47**, 301) (9 g.) and finely divided potassium (1·6 g.) in pure anhydrous benzene (70 c.c.) was heated under reflux on the water-bath for 138 hours with β-6-methoxy-1-naphthylethyl bromide (8·4 g.). The product was treated with ice-water, and the benzene solution separated, ether being used to complete the extraction. The combined extracts were washed with brine, dried, and concentrated. Vacuum distillation of the residue gave unchanged ethyl methylcyclopentanonecarboxylate (5 g.), b. p. 120—124°/20 mm., unchanged methoxynaphthylethyl bromide (3·5 g.), b. p. 145—155°/0·15 mm., and the desired *keto-ester* (4·8 g.), b. p. above 210°/0·1 mm. The last fraction was redistilled, giving a viscous yellow oil, b. p. 212°/0·2 mm. (*Found : C, 75·6; H, 6·9. $C_{22}H_{26}O_4$ requires C, 74·6; H, 7·35%). The *semicarbazone* crystallised from methyl alcohol in small yellowish plates, m. p. 161—163° (Found : N, 9·8. $C_{23}H_{29}O_4N_3$ requires N, 10·2%).

7-Methoxy-1′-methyl-1 : 2-cyclopentenophenanthrene.—The foregoing keto-ester (1·9 g.) was boiled for 6 hours with sulphuric acid (37 c.c.) (equal volumes of concentrated acid and water). After cooling, ice was added, and the dark resinous product digested repeatedly with small quantities of ether. The washed and dried ethereal extract was distilled in a vacuum. The product, b. p. 150—160°/0·1 mm., crystallised from alcohol containing a little acetic acid in colourless plates (0·45 g.), m. p. 93—95°. This was treated, in alcoholic solution, with an equal weight of *s.*-trinitrobenzene. The resulting *complex* formed orange-yellow needles of constant m. p. 129° (Found : C, 62·9; H, 4·4. $C_{19}H_{18}O,C_6H_3O_6N_3$ requires C, 63·1; H, 4·5%). 7-*Methoxy*-1′-*methyl*-1 : 2-*cyclopentenophenanthrene*, regenerated by removal of the trinitrobenzene (stannous chloride), followed by high vacuum sublimation, formed colourless plates (from alcohol), m. p. 97·5—98° (Found : C, 86·7; H, 6·8; OMe, 12·1. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9; OMe, 11·8%).

Ethyl 2-(β-6′-Methoxy-1′-naphthylethyl)-4-methylcyclopentanone-2-carboxylate.—This was prepared exactly as described for the 5-methyl compound from a solution of potassium (1·5 g.) in ethyl 4-methylcyclopentanone-2-carboxylate (Dieckmann, *Annalen*, 1901, **317**, 78) (7·8 g.) and benzene (80 c.c.), followed by addition of methoxynaphthylethyl bromide (8·6 g.), boiling being continued for 66 hours. The desired *keto-ester* (6·1 g.) formed a pale yellow, very viscous liquid, b. p. about 205°/0·05—0·1 mm. (*Found : C, 74·2; H, 7·4. $C_{22}H_{26}O_4$ requires C, 74·6; H, 7·35%).

7-Methoxy-2′-methyl-1 : 2-cyclopentenophenanthrene.—Cyclisation and dehydrogenation was effected by 5 hours' boiling of the above keto-ester (1·6 g.) with sulphuric acid (1 : 1 by volume; 38 c.c.). After isolation as described in the preceding case, the product (1 g. of distillate, b. p. 160—170°/0·1—0·2 mm.) was dissolved in hot alcohol (15 c.c.). The leaflets which separated on cooling were rapidly collected (long standing gave also some granular impurity) and had m. p. 134—135°. Purification through the *s.*-trinitrobenzene complex was effected in the customary way, the resulting 7-*methoxy*-2′-*methyl*-1 : 2-*cyclopentenophenanthrene* forming small

colourless needles (from alcohol), m. p. 136·5—137·5° (Found : C, 87·2; H, 7·0; OMe, 11·4. C$_{19}$H$_{18}$O requires C, 87·0; H, 6·9; OMe, 11·8%). The s.-*trinitrobenzene* complex crystallised from alcohol in microscopic golden-orange needles, m. p. 132—133°, depressed by the analogous derivative of 7-methoxy-3'-methyl-1 : 2-*cyclo*pentenophenanthrene (Found : C, 63·0; H, 4·4. C$_{19}$H$_{18}$O,C$_6$H$_3$O$_6$N$_3$ requires C, 63·1; H, 4·5%).

Synthesis of 7-Methoxy-3'-methyl-1 : 2-cyclopentenophenanthrene.

1-(β-6′-*Methoxy*-1′-*naphthylethyl*)-2-: 5-*dimethyl*-Δ^1-*cyclopentene*.—2 : 5-Dimethyl*cyclo*-pentanone (Cornubert and Borrel, *loc. cit.*) (5 g.) was added to an ice-cold Grignard solution prepared from β-6-methoxy-1-naphthylethyl bromide (8·8 g.), magnesium turnings (0·8 g.), and anhydrous ether (25 c.c.). After an hour at room temperature and then ¼ hour's boiling, the product was decomposed with ice and ammonium chloride, and the ethereal solution washed, dried, and distilled. There were obtained unchanged ketone (2·8 g.), b. p. 60°/20 mm. (semi-carbazone, m. p. 189—191°), the desired carbinol (3 g.), b. p. 160—200°/0·5 mm., and a residue of dimethoxydinaphthylbutane (2 g.) (compare Part III). The crude carbinol was heated for an hour at 160° with potassium hydrogen sulphate (4·5 g.), and the product isolated and distilled (2·2 g.; b. p. 164—169°/0·4 mm.). The *picrate* of 1-(β-6′-*methoxy*-1′-*naphthylethyl*)-2 : 5-*dimethyl*-Δ^1-*cyclopentene* formed an orange-yellow crystalline powder, m. p. 80—82° (Found : C, 60·8; H, 5·3. C$_{20}$H$_{24}$O,C$_6$H$_3$O$_7$N$_3$ requires C, 61·3; H, 5·35%).

7-*Methoxy*-1 : 3′-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-*cyclopentenophenanthrene*.—Cyclisation of the olefin (2 g.) in carbon disulphide (20 c.c.) by aluminium chloride (2 g.) was complete at 0° in 5 hours. The product, b. p. 175°/0·2 mm., gave a *picrate*, which crystallised from methyl alcohol in orange-red needles, m. p. 87—88° (Found : C, 60·2; H, 5·0; OMe, 6·1. C$_{20}$H$_{24}$O,C$_6$H$_3$O$_7$N$_3$ requires C, 61·3; H, 5·35; OMe, 6·1%). This picrate had a strong tendency to dissociate when recrystallised, which probably accounts for the low value for carbon. The s.-*trinitrobenzene* complex, prepared from the liquid methoxy-compound regenerated from the picrate, formed small orange crystals (from alcohol), m. p. 98° (Found : C, 63·2; H, 5·6. C$_{20}$H$_{24}$O,C$_6$H$_3$O$_6$N$_3$ requires C, 63·25; H, 5·5%).

7-*Methoxy*-3′-*methyl*-1 : 2-cyclo*pentenophenanthrene* (VIII).—The pure 1 : 3′-dimethyltetra-hydro-compound (0·15 g.) was heated with selenium (0·3 g.) at 300—310° for 15 hours. Purific-ation of the crystalline product was effected as with the *cyclo*pentenophenanthrene derivatives obtained from the hormones. 7-*Methoxy*-3′-*methyl*-1 : 2-cyclo*pentenophenanthrene* formed small colourless plates, m. p. 146·5—148·5° (Found : C, 87·1; H, 6·7. C$_{19}$H$_{18}$O requires C, 87·0; H, 6·9%). The mixed m. p. with the methoxydimethyl*cyclo*pentenophenanthrene prepared from oestrone was 143·5—144·5° (to a cloudy liquid). The s.-*trinitrobenzene* complex of this synthetic 3′-methyl compound had m. p. 135·5—136·5° (Found : C, 62·7; H, 4·5. C$_{19}$H$_{18}$O,C$_6$H$_3$O$_6$N$_3$ requires C, 63·1; H, 4·5%).

Synthesis of 7-Methoxy-3′ : 3′-dimethyl-1 : 2-cyclopentenophenanthrene (V).

2 : 2-Dimethyl*cyclo*pentanone was prepared from 2-methyl*cyclo*pentanone (Cornubert and Borrel, *loc. cit.*) by methylation with sodamide and methyl iodide (Haller and Cornubert, *Compt. rend.*, 1914, **158**, 300). In order to obtain good results it was necessary to proceed as follows : Finely powdered sodamide (12 g. = 50% excess) was added gradually to 2-methyl*cyclo*pentanone (20 g.) diluted with anhydrous ether (200 c.c.). After evolution of ammonia had ceased, methyl iodide (42 g.) was added dropwise; the mixture then boiled spontaneously and continued to do so for ¼ hour. The reaction was completed by 3 hours' heating on the water-bath. During the whole of this series of operations the mixture was stirred vigorously. The resulting 2 : 2-dimethyl*cyclo*pentanone (16·5 g.) had b. p. 143—145°, and gave a semicarbazone, m. p. 189—191° (lit., 193°). Haller and Cornubert (*loc. cit.*) state that methylation of this ketone gives a mixture of 2 : 2 : 5-trimethyl- (b. p. 151—152°) and 2 : 2 : 5 : 5-tetramethyl- (b. p. 155—156°) *cyclo*pentanones, which they claim to have separated by fractional distillation. These b. p.'s are so close that separation must be very difficult. By methylation of the dimethyl ketone in the manner described above we obtained a product, b. p. 150—152°, which gave (in poor yield) a semicarbazone which crystallised in well-formed needles and had constant m. p. 163·5—164·5° (the m. p. given in the literature for 2 : 2 : 5-trimethyl*cyclo*pentanone semicarbazone is 150—151°). However, analysis showed that our semicarbazone was not a pure compound, although probably consisting mostly of the semicarbazone of the trimethyl ketone (Found : C, 57·85; H, 9·1; N, 23·0. C$_9$H$_{17}$ON$_3$ requires C, 59·0; H, 9·4; N, 22·9%).

In order to avoid complications due to the heterogeneous nature of our ketone we employed

another route to 2 : 2 : 5-trimethyl*cyclo*pentanone. For this purpose, 2 : 2-dimethyl*cyclo*-pentanone (22 g.) was condensed with ethyl oxalate (28·5 g.) in presence of sodium ethoxide (4·6 g. of sodium in 60 c.c. of alcohol) exactly as described by Kötz and Michels (*Annalen*, 1906, 350, 210; 1908, 358, 198) in an analogous case. The resulting *ethyl 2 : 2-dimethyl*cyclo*pentanone-5-glyoxylate* (27 g.), which was not converted by heat into the β-keto-ester, was purified by solution in cold dilute alkali, extraction of neutral material with ether, and then liberation of the free diketo-ester. It formed a colourless liquid, b. p. 141°/12 mm., which gave a brownish-red colour with ferric chloride (*Found : C, 61·3; H, 7·4. $C_{11}H_{16}O_4$ requires C, 62·2; H, 7·6%). This ester was hydrolysed by heating for an hour with an equal weight of potassium hydroxide in aqueous alcoholic solution. 2 : 2-*Dimethyl*cyclo*pentanone-5-glyoxylic acid*, pre-cipitated by hydrochloric acid, was recrystallised from water, ligroin, and finally water; it then formed colourless plates, m. p. 75—76°, and gave an intense brownish colour with ferric chloride (*Found : C, 58·4; H, 6·65. $C_9H_{12}O_4$ requires C, 58·1; H, 6·6%).

For methylation, the potassio-compound of the diketo-ester (from 5·3 g. of potassium and 24 g. of ester in 90 c.c. of benzene) was boiled for 5 hours with methyl iodide (21·5 g.), and then kept over-night at room temperature. *Ethyl 2 : 2 : 5-trimethyl*cyclo*pentanone-5-glyoxylate* (12 g.), isolated in the usual way, had b. p. 135°/10 mm. (*Found : C, 63·3; H, 8·0. $C_{13}H_{20}O_4$ requires C, 63·7; H, 8·0%).

This ester (9 g.) was boiled for 2 hours with concentrated hydrochloric acid (30 c.c.) and water (30 c.c.). The cold solution was saturated with ammonium chloride and extracted with ether. The resulting 2 : 2 : 5-trimethyl*cyclo*pentanone (3·6 g.) gave a semicarbazone, m. p. 149—150° (Found : C, 59·1; H, 9·05; N, 22·95%).

An ice-cold Grignard solution prepared from β-6-methoxy-1-naphthylethyl bromide (6·8 g.) was treated with 2 : 2 : 5-trimethyl*cyclo*pentanone (3·1 g.), and the whole boiled for 20 hours. The product was worked up in the usual way. The very incomplete reaction, presumably owing to enolisation of the ketone, led to the isolation of 5-*ethylnerolin* (3·2 g.; b. p. 120—130°/0·5 mm., 165°/10 mm.), which was purified through its orange *picrate*, m. p. 83—84° (Found : N, 9·7. $C_{13}H_{14}O,C_6H_3O_7N_3$ requires N, 10·1%), and then formed colourless prismatic needles, m. p. 54—55° (Found : C, 84·0; H, 7·55. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%).

The crude carbinol fraction (0·7 g.; b. p. above 190°/0·3 mm.) arising from this Grignard condensation was dehydrated † with potassium hydrogen sulphate (1 g.) at 160°, extracted with carbon disulphide (10 c.c.), and the ice-cold solution treated with anhydrous aluminium chloride (0·7 g.). After remaining over-night at 2—3°, the clear solution was poured off and shaken with water. The pale yellow gum remaining after removal of carbon disulphide was heated with selenium (0·1 g.) at 300—320° for 13 hours. The product was extracted with ether and distilled at 0·2 mm. from an air-bath at 200°. The distillate (50 mg.) was treated with an alcoholic solution of s.-trinitrobenzene (30 mg.). After being twice recrystallised from alcohol, the s.-trinitrobenzene complex formed golden-orange needles, m. p. 170—171·5°, not depressed by the analogous complex of the 7-methoxy-3′ : 3′-dimethyl-1 : 2-*cyclo*pentenophenanthrene prepared from oestrone. By reduction with stannous chloride there was obtained the dimethyl compound (V), which crystallised from methyl alcohol in colourless plates, m. p. 165—165·5°, not depressed by the specimen prepared from oestrone (yield, about 2 mg.). This specimen, and the one from oestrone, gave an identical series of colour changes with concentrated sulphuric acid.

Demethylation of 7-Methoxy-1-methyl-1 : 2 : 3 : 4-tetrahydro-1 : 2-cyclopentenophenanthrene.

The hydroxy-compound corresponding to this methoxy-compound, the synthesis of which was described in Part III, was required in order to investigate its oestrogenic activity. Attempts to effect demethylation by acid reagents led to dark coloured tars. By using the following procedure the pure hydroxy-compound was readily obtained, although demethylation was incomplete : The methoxy-compound (0·8 g.) was heated with sodium ethoxide (0·8 g. of sodium in 16 c.c. of alcohol) at 190—195° for 20 hours. The solution, after dilution with water, was extracted with ether. The clear aqueous solution was then acidified, and the phenol extracted with ether. The product (0·1 g.) was treated with benzoyl chloride in pyridine,

† We were, of course, fully aware of the possibility of methyl migration during the dehydration of the carbinol arising from the interaction of the trimethyl*cyclo*pentanone with the methoxynaphthylethyl-magnesium bromide. However, although one of the carbon atoms contiguous to the carbinol group is quaternary, the other is tertiary, and we were inclined to the belief that this would tend to promote normal dehydration, without migration. This view was justified by the results.

and the *benzoate* sublimed in a high vacuum at 170°. After recrystallisation from aqueous alcohol it formed colourless cubic crystals, m. p. 141—141·5° (Found : C, 84·05; H, 6·8. $C_{31}H_{24}O_2$ requires C, 84·2; H, 6·8%). The " non-acidic " fraction obtained from the original ethereal extract still contained a considerable amount of the phenol, of which 0·17 g. was isolated by trituration with light petroleum. The resulting *7-hydroxy-1-methyl-*1 : 2 : 3 : 4-*tetrahydro-*1 : 2-*cyclopentenophenanthrene* crystallised from light petroleum in colourless nodules, m. p. 131·5—132°, the same compound being obtained by hydrolysis of the benzoate described above (Found : C, 85·6; H, 7·9. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%). The liquors from the isolation of this phenol contained chiefly unaltered methoxy-compound, identified by conversion into its characteristic *s.*-trinitrobenzene complex.

98. *Primary Photochemical Reactions. Part VI. The Photochemical Decomposition of Certain Cyclic Ketones.*

By OLIVE D. SALTMARSH and RONALD G. W. NORRISH.

IN previous papers (Norrish and Kirkbride, J., 1932, 1518; Norrish, Crone, and Saltmarsh, J., 1933, 1533; 1934, 1456; Norrish and Appleyard, *ibid.*, p. 874) an examination of the primary photochemical change suffered by the vapours of simple ketones was described. It was concluded that, when light corresponding to the absorption band of the carbonyl group lying between *ca.* 3500 and 2000 Å.U. is absorbed, two types of decomposition are possible : (I) With short-chain ketones, the change typified by the photochemical decomposition of acetone occurs : $CH_3 \cdot CO \cdot CH_3 \longrightarrow C_2H_6 + CO$. (II) With long-chain ketones, a break may occur instead in the hydrocarbon chain, as with methyl butyl ketone, which decomposes almost quantitatively according to the equation :

$$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3 \longrightarrow CH_3 \cdot CO \cdot CH_3 + CH_3 \cdot CH{:}CH_2.$$
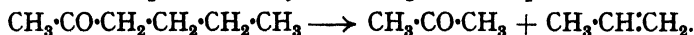
From methyl ethyl ketone, three paraffins were produced in nearly equal amounts, and the total paraffin was nearly equivalent to the carbon monoxide, the decomposition being represented to the extent of about 90% by the equation :

$$CH_3 \cdot CO \cdot C_2H_5 \longrightarrow \tfrac{1}{3}(C_2H_6 + C_3H_8 + C_4H_{10}) + CO.$$
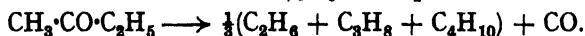
A further study of the fluorescence and absorption of acetone confirmed our view that decomposition of the type (I) arises from a primary change in which free radicals are produced, while that of type (II) does not. These conclusions have been confirmed in a very direct manner by Pearson (J., 1934, 1718), who isolated free radicals from acetone and methyl ethyl ketone, but *not* from methyl butyl ketone. The type of primary disruption associated with type (I) is itself of particular interest, for it appears that not one but both hydrocarbon radicals are ejected as a result of the absorption of a light quantum, to leave a normal ($^1\Sigma$) molecule of carbon monoxide : *

$$CH_3 \cdot CO \cdot C_2H_5 \longrightarrow CH_3 + C_2H_5 + CO - 78 \text{ kg.-cals.}$$
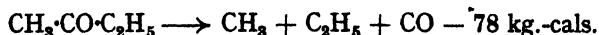
This follows from the equivalence of the hydrocarbons and carbon monoxide, which excludes the possibility of the polymerisation of such radicals as $\cdot CO \cdot C_2H_5$ and shows that, if they are formed at all, they must decompose spontaneously within a very short time.

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* The energy absorbed in the elimination of a single free radical corresponds to the thermal value of the C–C bond (*ca.* 89·5 kg.-cals.). To eliminate two free radicals we only require 78 kg.-cals., because the reorganisation of the carbonyl group (>CO) to carbon monoxide (C≡O) yields 101 kg.-cals. This point has already been fully discussed by one of us (Norrish, *Trans. Faraday Soc.*, 1934, **30**, 103).

The discovery of these two types of photochemical change made it of special interest to study in some detail the photolysis of cyclic ketones, for, with a ring of several carbon atoms, it is not apparent which of the two types of decomposition will intervene. Whatever the character of the reaction, however, it might be expected to throw fresh light on the mechanism of these changes.

In the present paper we examine the decomposition of *cyclo*-heptanone, -hexanone, and -pentanone. The first two give a high yield of cyclic hydrocarbon, together with a small quantity of its olefinic breakdown products, and an equivalent quantity of carbon monoxide. The last gives ethylene, isomeric butylenes, and carbon monoxide. Where a cyclic hydrocarbon of six or five carbon atoms is possible, this is readily formed, but, instead of *cyclo*butane, only its breakdown or isomerisation products are obtained.

These reactions may be summarised by the following scheme :

$$2CH_3 \cdot CH:CH_2 + CO \qquad [4\%] \qquad . \quad . \quad . \quad (2)$$

$$C_2H_4 + CH_3 \cdot CH:CH_2 + CO \quad [8\%] \qquad . \quad . \quad (4)$$

$$2C_2H_4 + CO \qquad [50\%] \qquad . \quad . \quad (5)$$

$$\begin{Bmatrix} CH_3 \cdot CH_2 \cdot CH:CH_2 \\ CH_3 \cdot CH:CH \cdot CH_3 \end{Bmatrix} + CO \quad [50\%] \quad . \quad . \quad (6)$$
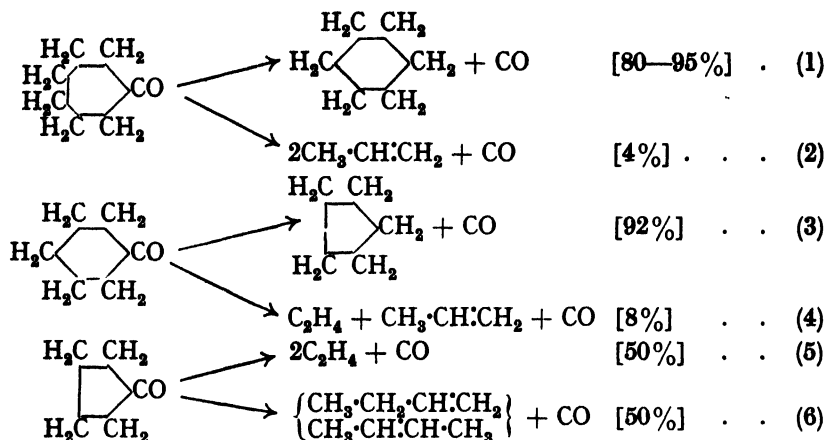
Hence, these cyclic ketones decompose primarily by a process of the first type, and the essential simplicity of the process affords further evidence of the simultaneous rupture of both bonds attached to the carbonyl, as has already been concluded on other grounds.

EXPERIMENTAL.

The apparatus employed was similar to that illustrated in Part IV (J., 1934, 874). 3—4 G. of the ketone were refluxed in a vacuum in a long-necked, quartz flask of 100 c.c. capacity. The attachment of the flask to the double-surface condenser was made by way of a water-cooled ground joint, lubricated by a thin film of " Apiezon " grease. The vapour in the neck at a pressure of 1—10 mm. was subjected to the full radiation of a vertical mercury-vapour lamp, while the liquid ketone was carefully protected from irradiation by covering the spherical part of the flask with asbestos paper. The gaseous products of decomposition collected mainly in a 1-litre globe, out of range of the radiation, and could be pumped off by way of a liquid-air trap and a manometer by means of a Toepler pump. The apparatus could also be evacuated by means of a " Hyvac " pump. When the irradiation was completed (3—30 hours, corresponding to the decomposition of 0·1—0·6 g. of ketone), the products were separated into three fractions by pumping off with the flask and trap cooled (1) in liquid nitrogen at − 192°, (2) in solid carbon dioxide and ether at − 78°, and (3) in ice and hydrogen chloride at − 30° or ice at 0°. The various fractions were analysed separately. Fraction (1) was practically pure carbon monoxide. Fraction (2) consisted solely of olefins, which were usually identified by explosion. Fraction (3) consisted of volatile liquids which were distilled into small weighed tubes, and these were sealed off and re-weighed. These liquids proved to be hydrocarbons, and were identified by a determination of their vapour pressures, b. p.'s, and f. p.'s. To determine their vapour pressures, they were distilled into the trap, isolated from the rest of the apparatus by a stopcock, and allowed to warm to room temperature, the pressure being read off on the manometer. The boiling points were determined by the micro-method of Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, **32**, 897) and generally found to be steady.

Materials.—(1) *cyclo*Heptanone, prepared by Mosettig and Burger's method (*ibid.*, 1930,

52, 2456), *viz.*, addition of *cyclo*hexanone to an ethereal solution of diazomethane, was purified through its bisulphite compound and finally dried over calcium chloride; b. p. 180°.

(2) *cyclo*Hexanone was obtained by similar purification of the commercial product; b. p. 153—154°.

(3) *cyclo*Pentanone, prepared by the dry distillation of adipic acid in the presence of a small quantity of barium hydroxide ("Organic Syntheses," 1925, 5, 37), was similarly purified; b. p. 129—130°.

Decomposition of cycloHeptanone.—Since the vapour pressure of the ketone is very low, 20—30 hours' irradiation was required for the accumulation of sufficient products for satisfactory analysis. Fraction (1) consisted entirely of carbon monoxide. Fraction (2) was small in amount, and completely absorbed by bromine : it was shown by explosion to be propylene. Fraction (3) (0°) was a liquid of high vapour pressure (Found, by micro-method : C, 87·4; H, 13·9. Calc. for C_6H_{12} : C, 85·7; H, 14·3%). Its physical constants are here compared with those of *cyclo*hexane :

	Vapour pressure, mm.*		B. p.	F. p.
	At 18°.	At 47°.		
*cyclo*Hexane	74	230	81°	6·5°
Fraction (3)	77	223	77—81	3·5

A mixed m. p. gave 5·7°. The liquid was inert, immiscible with water, and unaffected by reagents. A summary of the analytical results of two experiments is given below. In the first, the maximum quantity of *cyclo*hexane was extracted by distillation; in the second, no attempt was made at quantitative separation.

Time of illumination, hrs.	Products of decomposition (converted into c.c. at *N.T.P.*).			
	Total.	Fraction (1), CO.	Fraction (2). C_3H_6.	Fraction (3). C_6H_{12}.
34	69·3	32·7	2·7	24
23	30·1	21·6	0·5	8

According to the equations (1) and (2), the volume of carbon monoxide formed in the decomposition should be equal to that of the *cyclo*hexane plus half that of the propylene. In the first experiment, therefore, this should be 25·35 c.c., as compared with 32·7 c.c. found; this deficiency, however, is not surprising in view of the difficulty of fractionating the last traces of *cyclo*hexane from the unchanged *cyclo*heptanone. Since the yield of propylene fixes the amount of ketone which decomposes according to equation (2), the proportions of the two directions of breakdown are calculated to be as shown on p. 456.

Decomposition of cycloHexanone.—After irradiation of the vapour of the ketone for 4—5 hours, the gaseous products were pumped off in three fractions at the same temperatures as before. Fraction (1) consisted of pure carbon monoxide; (2) was completely absorbed by bromine water, and was shown by explosion to consist of equal volumes of ethylene and propylene; (3) consisted of a liquid of high vapour pressure, which was distilled off and weighed (f. p. —95·5°, b. p. 49·5—50·5°, whereas the data recorded for *cyclo*pentane are —93·3° and 49·5°). The liquid was immiscible with water and quite inert to all reagents. In accordance with the rest of the analytical data, there is no doubt as to its identity with *cyclo*pentane. A summary of the analytical results is given :

Time of illumination, hrs.	Products of decomposition (converted into c.c. at *N.T.P.*).			
	Total.	Fraction (1). CO.	Fraction (2). $C_2H_4 + C_3H_6$.	Fraction (3). *cyclo*Pentane.
4	207·3	98·9	17·3	91·0
4·5	208·3	118·2	15·1	75·0

According to the equations (3) and (4), the volume of carbon monoxide should be equal to that of *cyclo*hexane plus half the total olefins. For the first experiment, this should be 99·65 c.c. (cf. 98·9 c.c.); in the second experiment no attempt was made to obtain a quantitative yield of *cyclo*pentane, the liquid being fractionated several times in the decomposition apparatus in order to ensure its absolute purity for the determination of b. p. and f. p. This accounts for the deficiency. It is apparent that about 90% of the decomposition followed equation (3) while 8—9% followed equation (4).

* For the determination at 47° the connecting tubing and manometer were heated to 60° by winding them with a nichrome wire and asbestos wool, and passing a suitable current. The trap containing the liquid was then heated to 47° by a bath.

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Decomposition of cyclo*Pentanone.*—The analysis of the products proved somewhat more complicated in this case. In view of the previous results, it was expected that some *cyclo*butane might be formed, but none was found; instead, there resulted a considerable quantity of butylene, which was isolated partly as gas, and partly as liquid.

The ketone was irradiated for 3—5 hours, and the products separated as before. Fraction (1) was pure carbon monoxide. Fraction (2) was completely absorbed by bromine water, and shown by explosion to be a mixture of ethylene with some higher olefinic hydrocarbons. In order to identify the latter, the gas was allowed to expand into a dry bulb cooled in a freezing mixture, and its pressure–volume isothermals determined at temperatures from $0°$ to $-20°$. The gas contained a constituent condensable at $-20°$ and having a vapour pressure of about 250 mm. at this temperature. The b. p. of Δ^{β}-butylene is $1\cdot4°$, and the vapour pressures of both ethylene and propylene are of the order 200 mm. at temperatures $20°$ below their b. p.'s; thus we may assume that the vapour pressure of Δ^{β}-butylene, which is not recorded in the literature, will be of the order 200 mm. at $-20°$, and this compound probably forms a considerable constituent of fraction (2).

A liquid of high vapour pressure remained in the quartz flask after the gaseous products had been removed, and was separated as fraction (3) by distillation from the unchanged *cyclo*pentanone at $-20°$. The vapour density of the liquid was determined by measuring the pressure of the unsaturated vapour in a part of the apparatus of known volume, and then condensing it into a small previously weighed tube attached to the apparatus by a rubber joint, sealing off, and weighing. The vapour density determined in this way in two experiments was $23\cdot7$ and $27\cdot5$ (Calc. for $C_4H_8 : 28$). Part of the liquid was next allowed to evaporate into a gas burette, and treated with bromine water, over 95% being absorbed instantaneously. *cyclo*Butane does not react with bromine water (Willstätter and Bruce, *Ber.*, 1907, **40**, 3988), and we therefore conclude that the product is a butylene. Its m. p., $-96°$, was between that of Δ^{α}- and Δ^{β}-butylene ($-130°$ and above $-78°$ respectively), and it may therefore be taken to be a mixture of these isomerides, the presence of butylene in fraction (2) being due to the volatility of the liquid, which is still unfrozen at $-78°$.

The analysis of the products of decomposition was :

Time of irradiation, hrs.	Volumes of products (converted into c.c. at *N.T.P.*).				
	Total.	Fraction (1). CO.	Fraction (2).		Fraction (3). C₄H₈ (liquid).
			C_2H_4.	C_4H_8 (gas).	
4	106	39·5	66·6		6·05
5*	358·5	152	122·5	65·5	17·5
4·5	136	51·4	62·2	15·6	6·8

* A greater intensity was used in this experiment.

According to the equations (5) and (6), the volume of carbon monoxide should be $144\cdot2$ and $53\cdot5$ c.c. in the second and the third experiment, respectively (Found : 152, 51·4 c.c.); the agreement is thus satisfactory. It will be seen that butylene and ethylene are formed approximately in the ratio $1 : 2$, and that therefore each of the two reactions is equally probable.

DISCUSSION.

The type of decomposition thus found for the simple cyclic ketones agrees well with that found for short-chain, open ketones. There is no tendency for a *primary* rupture of the hydrocarbon part of the ring, similar to that occurring with long-chain, open ketones. In this case, however, the possibility of eliminating a molecule of acetone cannot be visualised without the creation of acetylenic hydrocarbons. In conformity with the decomposition of simple mixed ketones, we see that the carbon monoxide must be eliminated as a result of the simultaneous or nearly simultaneous rupture of both links, for there is no tendency to any polymerisation of heavy radicals, and the carbon monoxide is equivalent to the hydrocarbons produced.

It is notable that, although the two higher cyclic ketones each gave about 90% decomposition to the lower *cyclo*paraffin together with a small amount of olefin, yet *cyclo*pentanone yielded no detectable *cyclo*butane, but gave butylene and ethylene instead. This difference is explained by the different stabilities of the *cyclo*paraffins, the heat effects for the reactions $[CH_2]_nCO \longrightarrow [CH_2]_n + CO$ being calculated from established thermal data to be $31\cdot5$, $33\cdot6$, and $-2\cdot2$ kg.-cals. for $n = 6$, 5, and 4 respectively. It is therefore seen that the

reactions are either considerably exothermic, or thermoneutral. The magnitude of the light quantum is of the order 100 kg.-cals. per g.-mol., and this amount of energy plus the heats of reaction must appear in the products. Hence, it is probable that the cyclic paraffins will be liberated in a high state of thermal vibration. We may conclude that this thermal energy is sufficient entirely to decompose or isomerise the unstable *cyclo*-butane (or to prevent its ever being formed), while the two higher homologues are nearly proof against its disruptive effects : even here, however, some 5% of the cyclic hydrocarbons are decomposed to olefins. It is not possible to generalise further about the various types of photochemical decomposition exhibited by ketonic substances. Preliminary experiments upon other typical ketones indicate that the full range of possibilities has not yet been disclosed. It may be affirmed, however, that the remarkable simplicity and variety attending these and analogous decompositions make the photochemistry of the carbonyl group a study of fundamental importance.

SUMMARY.

The photodecomposition of the vapours of *cyclo*-heptanone, -hexanone, and -pentanone has been studied in the full light of the mercury lamp. The ketones absorb between 3500 and 2000 Å.U. The equations summarising the results are given on p. 456.

In accordance with previous work, the primary change is conceived as a simultaneous or nearly simultaneous rupture of the two bonds joining the carbonyl group to the ring, carbon monoxide being eliminated. Since all the changes are themselves either exothermic or thermoneutral, the energy of the light quantum must appear in the products. As a result, it is suggested that thermal vibrations appear in the hydrocarbon ring, which result in the slight decomposition of the *cyclo*hexane and *cyclo*pentane to olefins, and the almost complete decomposition or isomerisation of the *cyclo*butane.

99. *The Planar Configuration for Quadricovalent Nickel, Palladium, and Platinum.*

By E. G. Cox, F. W. Pinkard, W. Wardlaw, and K. C. Webster.

IN 1931, Pauling (*J. Amer. Chem. Soc.*, 53, 1367) applied wave-mechanical methods to the problem of covalent linkages and showed that for quadricovalent atoms in which electrons from the first two sub-groups (*s* and *p*) of the outer level were used in chemical bonds, the stable configuration is tetrahedral. In the case of the transition elements, however, one or more electrons used in binding may belong to the *d* sub-group of the incomplete inner level, and in these cases the four covalencies may be distributed in a plane. Moreover, since the *d* electrons are chiefly responsible for the magnetic moment of the atom, sharing of them should reduce this property so that four-covalent nickel compounds should be diamagnetic. Pauling's conclusions have been criticised by Heisenberg (see *Ann. Reports*, 1931, 28, 367) and others, but appear to be essentially correct. The point to be recognised in connection with his work is that the results are probably permissive, *i.e.*, they show that the metals in question may have, but not necessarily must have, a planar distribution of valencies. These conclusions are particularly interesting in the case of nickel, for Werner did not include this metal in the list of elements which he considered could have planar structures for their quadricovalent compounds. Chemical and physical evidence has definitely established planar structures for quadricovalent platinum and palladium. With nickel, apart from crystallographic evidence, Pauling's prediction seems to be supported by Sugden's proof (*J.*, 1932, 246) that the nickel derivative of benzylmethylglyoxime can occur in two forms which are interconvertible and diamagnetic. Already, in 1911, Tschugaeff (*Chem. Zentr.*, 82, i, 871) had discovered

that the nickel derivative of monoethylglyoxime could occur in two isomeric forms, also interconvertible, but he did not consider it necessary to make any assumptions as to the distribution of the nickel valencies to explain this isomerism. Nevertheless, these experimental observations of Tschugaeff and Sugden certainly suggest that for quadricovalent nickel a planar structure is probable.

Recently, Brasseur, de Rassenfosse, and Piérard (*Z. Krist.*, 1934, **88**, 210) have shown barium nickelocyanide tetrahydrate, $BaNi(CN)_4,4H_2O$, to be isomorphous with the corresponding platinocyanide and palladocyanide. By means of intensity measurements they were able to find the positions of the barium and nickel atoms, but they were unable to prove that the four Ni–CN bonds are coplanar, or to find the position of the water molecules; *i.e.*, the possibility of the existence in the crystal of the octahedral complex $Ni(CN)_4(H_2O)_2$ was not rigorously eliminated.

With the object of proving conclusively that quadricovalent nickel may be planar and diamagnetic, we have investigated the salicylaldoxime derivatives of platinum, palladium, and nickel. These quadricovalent compounds may have structures (I) or (II), but (I) is considered the more probable by Brady (*J.*, 1931, 105). The conclusions which follow hold good, however, irrespective of the precise structure of the chelate groups.
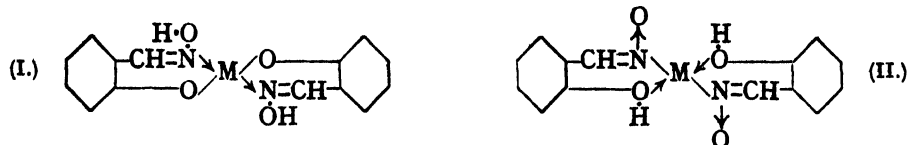
The nickel compound is well known, and the palladium derivative has recently been suggested for the microchemical estimation of this metal, but the platinum compound had not been investigated. We find that the product of the reaction between a solution of potassium chloroplatinite and salicylaldoxime is a mixture of the *platinum* derivative, $Pt(C_7H_6O_2N)_2$, and *disalicylaldoximinoplatinous chloride* $Pt(C_7H_7O_2N)_2Cl_2$. All the compounds $M(C_7H_6O_2N)_2$, where M = Ni, Pd, Pt, crystallise well without solvent of crystallisation; they are almost insoluble in water, but soluble in carbon tetrachloride, chloroform, and benzene. Molecular-weight determinations prove them to be monomeric, and undoubtedly their properties indicate that they have covalent structures.

The nickel and the palladium compound form good crystals which are isomorphous. *X*-Ray examination of them has shown that the molecule in each case possesses a centre of symmetry, and therefore has a planar *trans*-configuration. This result follows from space-group considerations, and is thus quite certainly established without the necessity of employing intensity measurements, which, unless very exhaustive, are liable to misinterpretation in the case of complex compounds of this nature. In all cases, *cis*- and *trans*-isomerides could exist. The nickel compound does, in fact, occur in a second crystalline form, but it appears to be merely a dimorphous form of the *trans*-isomeride. The platinum derivative occurs in two modifications, neither of which is isomorphous with the nickel or the palladium compound. One form has definitely a planar *trans*-configuration; the other is not dimorphous but has a complicated tetragonal structure, with 32 molecules of disalicylaldoximeplatinum to the unit cell. The molecules are asymmetric, as would be expected for the *cis*-isomeride on the *trans*-pairing hypothesis or a tetrahedral configuration. The copper derivative has also been examined. This has a structure quite different from that of any of the others mentioned, but owing to the poorness of the crystals it has not been worked out completely.

The planar distribution for the valencies in this quadricovalent nickel compound having been established, it was obviously an excellent case to test the validity of Pauling's deduction that it should be diamagnetic. Dr. L. C. Jackson, of the University of Bristol, very kindly examined this compound and finds the deduction to be correct.

EXPERIMENTAL.

Disalicylaldoximenickel.—An aqueous solution of nickel chloride (2 g. in 250 ml.) was mixed with a slight excess of aqueous salicylaldoxime (2·5 g. in 200 ml.), and then solid sodium acetate

(4 g.) stirred in. The bright green precipitate was washed with water and dried over phosphoric anhydride. The dried product was dissolved in hot chloroform, and emerald-green crystals slowly separated on standing (Found : Ni, 17·79; N, 8·6. Calc. : Ni, 17·74; N, 8·5%).

The molecular weight was determined ebullioscopically in chloroform. The following results were obtained (M, calc. : 330·7) :

c (g./1000 ml.)	5·420	6·670
Δt	0·045°	0·050°
M	313·2	346·8

Disalicylaldoximepalladium.—To an aqueous solution of potassium chloropalladite (1 g. in 70 ml.) was added a slight excess of aqueous salicylaldoxime (1 g. in 70 ml.). The bright yellow precipitate which immediately formed was purified and recrystallised as above. The orange-yellow crystals are isomorphous with the nickel compound (Found : Pd, 28·19; N, 7·6. Calc. : Pd, 28·17; N, 7·4%).

The molecular weight was determined as above (M, calc. = 378·8) :

c (g./1000 ml.)	4·418	3·698
Δt	0·032°	0·025°
M	358·8	384·7

Monosalicylaldoximepalladous Chloride.—Aqueous solutions of potassium chloropalladite (2 g. in 250 ml.) and salicylaldoxime (1 g. in 100 ml.) were cooled in ice, and the latter added to the former with constant stirring. The chocolate-coloured precipitate was washed, dried, and extracted with 15 ml. of cold acetone, giving an orange-red solution. Light petroleum was added to this solution until no further precipitation occurred, and the brown amorphous powder which had been thrown out was filtered off as rapidly as possible [Found : Pd, 38·8. Pd(C₇H₆O₂N)Cl requires Pd, 38·4%]. This *compound* is decomposed by further addition of salicylaldoxime solution to give the normal disalicylaldoximepalladium. The filtrate on standing deposits crystals of the latter, together with some palladous chloride. The probable structure of this derivative is

$$C_6H_4 \big\langle \substack{-O- \\ CH=N} \big\rangle Pd \big\langle \substack{Cl \\ Cl} \big\rangle Pd \big\langle \substack{-O- \\ N=CH} \big\rangle C_6H_4$$
$$\substack{| \\ OH} \qquad\qquad \substack{| \\ OH}$$
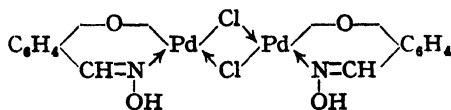
Disalicylaldoximeplatinum.—Aqueous solutions of potassium chloroplatinite (2 g. in 200 ml.) and salicylaldoxime (1·5 g. in 150 ml.) were mixed and kept for 48 hours; the yellow precipitate which had formed was then filtered off, and the filtrate set aside for a further crop. The precipitate had a platinum content of about 37% and was a mixture of disalicylaldoximeplatinum and disalicylaldoximinoplatinous chloride. This was dissolved in cold acetone and the solution allowed to evaporate in a dark cupboard, since light causes decomposition. The *disalicylaldoximeplatinum* separates out in yellow anhydrous crystals, leaving the very soluble disalicylaldoximinoplatinous chloride in solution. After a further recrystallisation from acetone or carbon tetrachloride, the crystals were pure [Found : Pt, 41·83; N, 6·1. Pt(C₇H₆O₂N)₂ requires Pt, 41·78; N, 6·0%]. This compound crystallises in two forms; the crystals usually obtained are monoclinic prisms, but occasionally a darker yellow type separates in the form of tetragonal needles. The two forms are readily interconvertible merely by dissolving them in acetone or carbon tetrachloride and allowing the solution to crystallise, whereupon either form may separate out. The type of crystal obtained does not depend on temperature, and there seems to be no criterion by which one can forecast which form will separate from solution.

The molecular weight was found ebullioscopically in acetone, the monoclinic crystals being used as starting point (M, calc. = 467·2) :

c (g./1000 ml.)	6·513	8·023
Δt	0·029°	0·041°
M	498·6	434·4

A solution of the tetragonal form in acetone was prepared, and the molecular weight determined by Barger's method, with naphthalene as the standard substance. It was found that the vapour pressure of a 0·4016% disalicylaldoximeplatinum solution was greater than that of a 0·00938N- and less than that of a 0·00816N-solution of naphthalene. Hence the molecular weight lies between 428 and 496 (calc., 467·2).

Disalicylaldoximinoplatinous Chloride.—The first product from the reaction between salicylaldoxime and potassium chloroplatinite was extracted with boiling carbon tetrachloride until

the extract was almost colourless. The pale greenish-yellow residue was dried over phosphoric anhydride [Found : Pt, 35·89; N, 5·2. $Pt(C_7H_7O_2N)_2Cl_2$ requires Pt, 36·13; N, 5·1%]. The presence of chlorine was also proved.

It is readily soluble in acetone and alcohol, giving pale yellow solutions which decompose on standing and do not crystallise. Sodium acetate solution reacts with this compound to give disalicylaldoximeplatinum and sodium chloride. The former is extracted from the product of reaction by means of hot carbon tetrachloride.

Crystallographic and X-*Ray Results.*—X-Ray investigations were carried out by means of single-crystal rotation and oscillation photographs using $Cu_{K_α}$ radiation.

Disalicylaldoximepalladium. Crystals prepared as above were found to be monoclinic holohedral combinations of $a\{100\}$, $r\{101\}$, $R\{10\bar{1}\}$, and $m\{110\}$, R predominating, and the crystals being elongated along the b-axis. The absence of a pyro-electric effect (tested for by the liquid-air method) confirmed the holohedral symmetry both of this compound and of the isomorphous nickel derivative. Angles observed : $a\{100\} : r\{101\} = 40° 21'$; $a\{100\} : R\{10\bar{1}\} = 67° 09'$; $a\{100\} : m\{110\} = 69° 11'$; whence $a : b : c = 2·81 : 1 : 2·10$ and $β = 110° 42'$.

From X-ray measurements, $a = 13·63$, $b = 4·89$, $c = 10·20$ Å.U., $β = 110° 30'$ ($a : b : c = 2·79 : 1 : 2·09$).

With two molecules in the unit cell, $d = 1·97$ g./c.c. (obs. = 1·96).

Reflections not occurring : $\{h0l\}$ when $h + l$ is odd, $\{0k0\}$ when k is odd; whence the space-group is $P2_1/m(C_{2h}^5)$. Each molecule in the crystal has therefore a centre of symmetry, so that the co-ordinated groups are arranged in *trans*-positions, the four metal valencies being coplanar.

Disalicylaldoximenickel. As normally occurring, this is isomorphous with the palladium compound, corresponding axes in the two cases being almost identical : d (calc. for two molecules per unit cell) = 1·73 (obs. = 1·74). The space-group is $P2_1/m(C_{2h}^5)$, and the molecule has a centre of symmetry. This compound is sometimes obtained in irregular thin plates, which give X-ray photographs closely similar to those of the usual crystals, indicating that the substance is dimorphous.

Disalicylaldoximeplatinum. This exists in two crystalline forms, neither of which is iso-morphous with the palladium or the nickel compound.

(a) *trans*-Form. The crystals are monoclinic prisms, being combinations of $c\{001\}$, $b\{010\}$, $p\{011\}$, $a\{100\}$, and $r\{101\}$; usually elongated along $[a]$ with p predominating, but sometimes elongated along $[c]$.

X-Ray measurements give $a = 5·79$, $b = 24·23$, $c = 4·53$ Å.U., $β = 97° 36'$; d (calc. for two molecules per unit cell) = 2·46 g./c.c. (obs. = 2·45).

Reflections not occurring : $\{h0l\}$ when $h + l$ is odd, $\{0k0\}$ when k is odd; therefore the space-group is $P2_1/m(C_{2h}^5)$, and the molecule has a centre of symmetry.

(b) The second form crystallises in ditetragonal bipyramidal needles $a\{100\}$ terminated by $\{h0l\}$.

From X-ray measurements, $a = 26·60$ and $c = 14·40$ Å.U. With 32 molecules in the unit cell, $d = 2·43$ g./c.c. (obs. = 2·42). The [111] axis is 20·1 Å.U., showing that the cell is body-centred, and since $\{110\}$ is halved, the space-group is probably $I4/amd(D_{4h}^{19})$. The molecules are asymmetric : this result, coupled with the observation that this form can be obtained under suitable conditions from the *trans*-isomeride by recrystallisation from either hot or ice-cold solutions, makes it very improbable that this is a dimorphous form of the *trans*-compound. On the other hand, the observed lack of symmetry is in accordance with expectations for a *cis*-isomeride with non-equivalent *cis*-valencies.

THE UNIVERSITY, EDGBASTON.   [*Received, February 21st*, 1935.]

100. *Mesityldimethylphosphine.*

By W. CULE DAVIES.

THIS *phosphine* has been found by measurements of reaction velocity to be more reactive towards alkyl halides than its arsenic analogue. The corresponding nitrogen compound, dimethylmesidine, gave no quaternary salt with methyl iodide (Hofmann, *Ber.*, 1872, **5**, 718). Thus, the order of reactivity of the o-substituted substances, phosphine > arsine > amine, is that which has already been found for the non-substituted bases (Davies and

Lewis, J., 1934, 1599), and is parallel with the dipole moments of the triphenyl bases (Bergmann and Schutz, *Z. physikal. Chem.*, 1932, **19**, 401) (Fig. 3).

The result is of interest in connexion with a suggestion of Lesslie and Turner (J., 1933, 1588) that mesityldimethylarsine (2 : 4 : 6-trimethylphenyldimethylarsine) should be more reactive towards alkyl halides than dimethylmesidine, because the larger arsenic atom is less under the steric influence of the *o*-methyl groups than the smaller nitrogen atom. Extending this view (see Fig. 1, atomic radii), it would appear that the corresponding bismuthine should be the most reactive base, and the phosphine of reactivity intermediate between those of the amine and the arsine. It is known, however, that bismuthines, generally, are non-reactive, and the present work has shown that the phosphine is the most reactive of all the bases of the elements of Group V*b*. Thus, the reactivities of the bases do not follow the order of the atomic radii of the central elements.

It is certain, therefore, that the principal factor determining the reactivity of the bases is one created by the polarisation of the central element. The substitution of *o*-groups diminishes the reactivity in each case, but the author considers that velocity measurements are not suitable, because of the magnitude of the above principal factor, for detecting differences in the effect of the *o*-groups in the various cases.

Fig. 1.   Fig. 2.   Fig. 3.
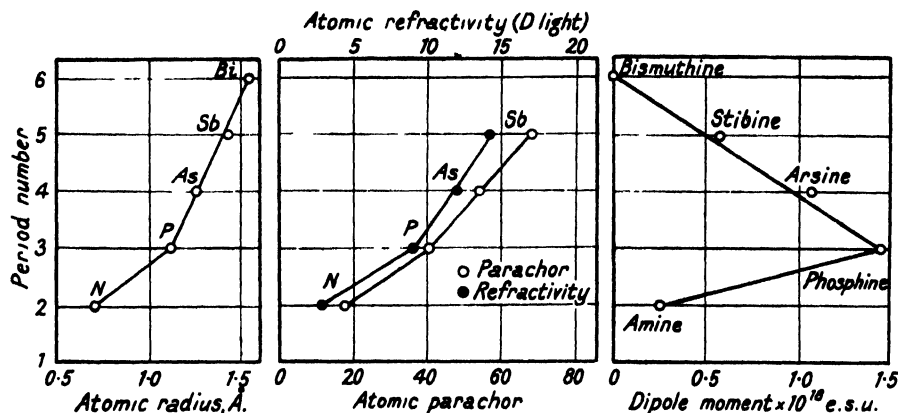
The atomic radii of the elements of Group V*b* are shown in Fig. 1. The value for nitrogen is given by Sidgwick (" The Covalent Link in Chemistry," 1933, p. 84), and the values for arsenic, antimony, and bismuth are from Hume-Rothery (*Phil. Mag.*, 1930, **10**, 217). In deriving the mean value for the atomic radius of phosphorus, P- = 1·11 Å., there have been used the results of Wierl (*Ann. Physik*, 1931, **8**, 521) for phosphorus trichloride, of Bergmann and Engel (*Z. physikal. Chem.*, 1931, **13**, 247) for phosphorus trichloride and tribromide, and of Passerini (*Gazzetta*, 1928, **58**, 655) for aluminium phosphide, to which a correction for the triple link has been applied. Values related to the atomic volumes, such as atomic refractivities and parachors, when plotted against the period number of the element, give similar curves (Fig. 2). Such atomic properties of the elements from phosphorus to bismuth fall on a straight line. The anomalous position of nitrogen is related to the fact that in the atoms of all the elements of the Group, except nitrogen, the valency electrons are separated from the helium nucleus by other stable electronic groupings.

EXPERIMENTAL.

(All thermometer readings are corrected.)

Mesityldichlorophosphine.—On account of the low yield in this case, the general method of isolation of a chlorophosphine by distillation at reduced pressure used in these laboratories was replaced by an extraction method, which is a modification of that used by Michaelis (*Annalen*, 1897, **294**, 35) in the preparation of this compound. A mixture of mesitylene (116 c.c.), phosphorus trichloride (73 c.c.), and commercial aluminium chloride (20 g.) was refluxed for 30 hours. The product was extracted with 250 c.c. of light petroleum. The combined extracts from several

preparations were distilled through an efficient column up to 145°/760 mm. The residue was fractionally distilled at reduced pressure, giving 15 g. of the dichlorophosphine, b. p. 156—157°/16 mm., from five preparations. The light petroleum, phosphorus trichloride, and mesitylene fraction was treated with excess of water; the hydrocarbon layer was dried over calcium chloride and distilled, light petroleum and mesitylene of sufficient purity for use in the chlorophosphine preparations being recovered.

Mesityldimethylphosphine.—A solution of 15 g. of the above dichlorophosphine in 50 c.c. of ether was slowly added to a cooled stirred Grignard reagent prepared from 35·5 g. of methyl iodide and 6 g. of magnesium. The mixture was boiled for 2 hours, cooled, and decomposed with aqueous ammonium chloride. The ethereal layer was dried over sodium sulphate, the ether expelled, and the residue fractionally distilled and then redistilled under reduced pressure. The tertiary *phosphine* (11 g.) had b. p. 133°/16 mm.; $d_4^{20°}$ 0·9570; $n_D^{20°}$ 1·5554; $[R_L]_D$ 60·46; $n_\gamma^{20°} - n_C^{20°}$ 0·0187 (Found : C, 73·5; H, 9·8. $C_{11}H_{17}P$ requires C, 73·3; H, 9·5%). The phosphine is not rapidly oxidised in the air.

The value of the atomic refractivity of phosphorus for the D line in the phosphine is 9·96, calculated by deducting the refractivities of two methyl groups and a mesityl group (Eisenlohr, *Z. physikal. Chem.*, 1910, 75, 585) from the Lorenz–Lorentz molecular refractivity. The optical exaltation due to the attachment of the mesityl group to the phosphorus atom is shown by comparison of the above value with the mean atomic refractivity of phosphorus of 9·14 in the trialkylphosphines (Jones, Davies, and Dyke, *J. Physical Chem.*, 1933, 27, 583).

Mesityltrimethylphosphonium iodide crystallised from water or alcohol in needles, m. p. 232° (Found : I, 39·4. $C_{12}H_{20}IP$ requires I, 39·4%), and *mesityldimethylethylphosphonium iodide* from alcohol in needles, m. p. 168° (Found : I, 37·6. $C_{13}H_{22}IP$ requires I, 37·8%).

An addition *compound* was obtained as red crystals by mixing the phosphine (1 c.c.) and carbon disulphide (2 c.c.) in benzene (3 c.c.) in the cold. It readily lost carbon disulphide in the air, but could be manipulated and preserved in an atmosphere containing carbon disulphide vapour. The compound dissolved with complete dissociation in the common solvents, but recombination took place when excess of carbon disulphide was added. The addition compound (Found : C, 56·3; H, 7·0. $C_{12}H_{17}S_2P$ requires C, 56·2; H, 6·7%) melted in a sealed tube at 58—59° to a colourless liquid, which solidified to a red crystalline mass on cooling.

Mesityldimethylarsine.—Considerable difficulty was experienced in obtaining the arsine of sufficient purity for quantitative measurements. The method of preparation differed in ·detail from that given by Lesslie and Turner (*loc. cit.*). An ethereal solution of 35 g. of dimethyl-iodoarsine was slowly added to a cooled stirred Grignard solution made from 66 g. of bromomesitylene and 10 g. of magnesium. The mixture was boiled for 2 hours, cooled, and cautiously treated with ammonium chloride solution. The ethereal layer was separated and dried, and the ether expelled. The residue was repeatedly fractionally distilled through a long packed column at reduced pressure, until an arsine fraction, b. p. 134—135°/17 mm., was obtained which gave almost a 100% yield of the methiodide when treated with excess of methyl iodide in solution in acetone–water (9 : 1 by vol.).

Velocity Measurements.—The rate of addition of methyl iodide and of ethyl iodide to the bases was measured by a method similar to that described by Davies and Lewis (*loc. cit.*), the following results being obtained.

Temp., 25°. Initial concentrations, 0·1 g.-mol. of the base and of the alkyl iodide/l. k (bimolecular), l./g.-mol./min.

Mesityldimethyl-base.	Alkyl iodide.	Solvent.	Mean k.	Time, mins., for 25% yield of I⁻.
Phosphine ·	MeI	Alcohol	0·890 *	3·7
,,	EtI	Acetone–water (9 : 1 by vol.)	— †	88
Arsine	MeI	,, ,, ,,	0·104	32
,,	,,	Alcohol	0·00944	353
,,	EtI	Acetone–water	— †	4650

* The -onium salt began to separate from solution when the reaction completed was approximately 70%.

† The bimolecular velocity coefficients drift.

The reaction between the phosphine and methyl iodide in acetone–water was too rapid to be measured by the method employed.

The author thanks the Chemical Society for a grant.

101. *Hydrocarbons from Neoergosterol.*

By G. A. D. Haslewood and (Miss) E. Roe.

The only crystalline product obtained in a long series of experiments aiming at the degradation of neoergosterol to a compound offering a reasonable hope of synthetic preparation was *neoergostatriol* (I). This was obtained in poor yield by oxidation of neoergosterol with perbenzoic acid, followed by hydrolysis of the crude resinous oxide.

Neoergostatetraene (II) was prepared by dehydration of the 22-dihydroneoergosterol of Windaus and Langer (*Annalen*, 1934, **508**, 105). Attempts to dehydrogenate (II) to the corresponding naphthalene derivative by a variety of methods gave indications that the required compound was probably formed, but it could not be isolated in the crystalline state.

Comparison of the absorption spectrum of the new neoergostatetraene and of neoergostapentaene (III) (Cook and Haslewood, *Chem. and Ind.*, 1934, **53**, 507) with that of the previously known neoergostatriene (IV) (Bonstedt, *Z. physiol. Chem.*, 1929, **185**, 165) has given strong evidence of the conjugation in (II) and (III) of the double bond in ring I with those comprising the neoergosterol benzene nucleus.
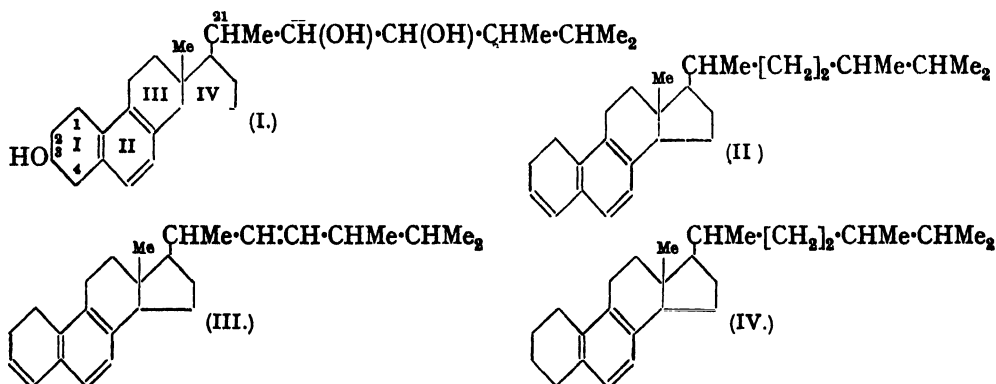
It is well known that when a chromophoric group, such as C:O or C:C, is directly linked to a benzene nucleus, the absorption spectrum differs considerably from that given by a compound in which such a group is separated from the nucleus (see, for example, Arnold and Kistiakovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1713; Ramart-Lucas, *Bull. Soc. chim.*, 1932, **51**, 289). The curves of the tetraene and the pentaene closely resemble each other, but differ widely from that of the triene. Hence it may be concluded that the double bond in the side chain of the pentaene has little influence on the absorption, and that the new double bonds arising in the preparation of both the tetraene and the pentaene are conjugated with the benzene nucleus. Differences of the same order are shown in the absorption spectra of styrene, allylbenzene, and δ-phenyl-Δᵅ-butene (Ramart-Lucas, *loc. cit.*). The spectroscopic technique used in our experiments was that described in a previous paper (J., 1934, 1727).

In view of the recent proof of the position of the hydroxyl group (at C_3) in ergosterol (Fernholz and Chakrovorty, *Ber.*, 1934, **67**, 2021), the spectroscopic evidence clearly shows that the tetraene and the pentaene are correctly represented by formulæ (II) and (III), from which it follows that the aromatic ring of neoergosterol must be ring II, a result in harmony with the conclusions of Honigmann (*Annalen*, 1934, **511**, 292) and of Dunn, Heilbron, Phipers, Samant, and Spring (J., 1934, 1576) with regard to the location in ring II of the nuclear double bonds of ergosterol.

The mode of dehydration of neoergosterol and dihydroneoergosterol is analogous to that of β-tetralol, which gives Δ¹-dihydronaphthalene (Strauss and Lemmel, *Ber.*, 1921, **54**, 25). The tetraene (II) and the pentaene (III) are resistant to reduction by sodium

and alcohol, in which respect they differ from Δ^1-dihydronaphthalene (compare Strauss and Lemmel, *Ber.*, 1913, **46**, 232).

A = Neoergostatetraene.
B = Neoergostapentaene.
C = Neoergostatriene.

Wave-length, Å.

Log α.
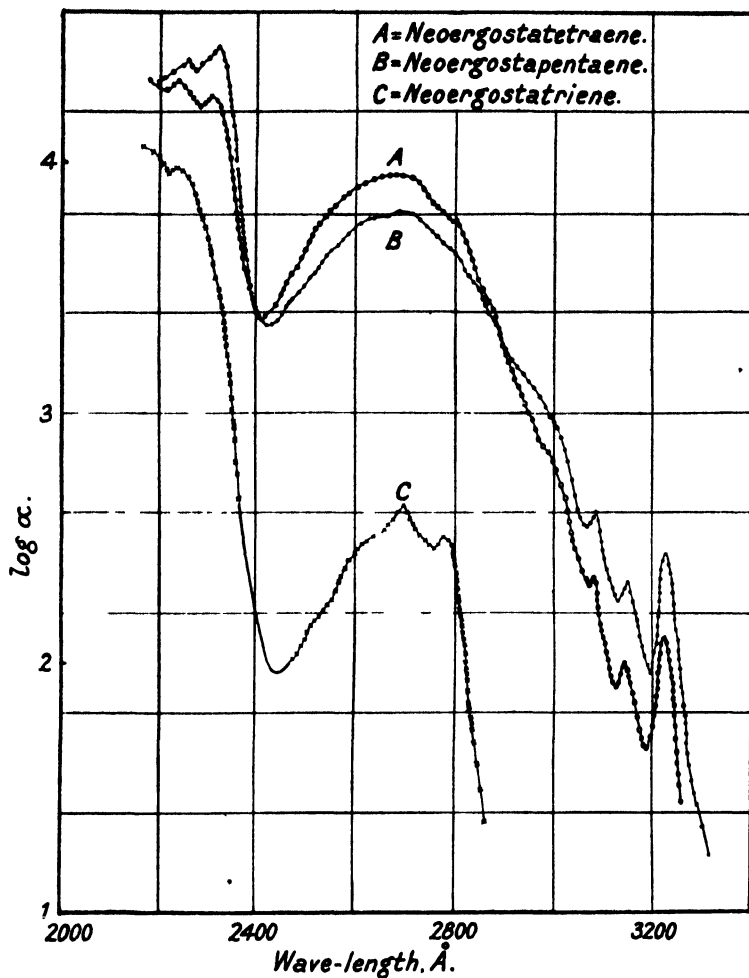
EXPERIMENTAL.

All analyses are microanalyses by Dr. A. Schoeller.

Dihydroneoergosterol was prepared by hydrogenation of (*a*) neoergosterol in moist ether or (*b*) neoergosteryl acetate in acetone (Windaus and Langer, *loc. cit.*), with palladium-black, during 5—7 hours at atmospheric temperature and pressure. Hydrogenation for a much longer period resulted, in both methods, in complete conversion into neoergostatriene (IV), m. p. 67—69°.

Dihydroneoergosterol, m. p. 141—143° (*lit.* 150°), showed no depression in m. p. with neoergosterol, and its 3 : 5-dinitrobenzoate (m. p. 216—218°) did not depress the m. p. (217—219°) of neoergosteryl 3 : 5-dinitrobenzoate. The dihydro-compound was readily distinguished from neoergosterol by its extremely slow absorption of bromine (in chloroform solution), and by its saturation towards perbenzoic acid, which showed a value for one double bond with neoergosterol.

Dehydration of Dihydroneoergosterol.—(*a*) *With phosphoric oxide.* Dihydroneoergosterol (0·1 g.) in benzene (0·5 c.c.) was refluxed for ¼ hour with phosphoric oxide (0·1 g.). The *product*, obtained by dilution with water, and benzene extraction, was crystallised from alcohol–benzene, sublimed at 260°/0·1—0·05 mm., and recrystallised from alcohol–benzene. It formed white

crystals, m. p. 187—190° (Found : C, 88·4; H, 10·9; M, Rast method, 626, 550. $C_{54}H_{84}$ requires C, 89·0; H, 11·0%; M, 729). Hence the substance is probably a dimeride.

(b) *With potassium hydrogen sulphate.* Dihydroneoergosterol (0·6 g.) was heated with freshly fused, finely powdered potassium hydrogen sulphate (1·2 g.) at 145—155° for 1 hour in a slow current of dry carbon dioxide. The product, obtained by ether extraction from the diluted mixture, was re-extracted with warm alcohol (to remove polymeric products which made distillation very difficult) and the residue obtained on evaporating the filtered alcoholic extract was distilled at 200—205°/0·1 mm. *Neoergostatetraene* (II) (0·2 g.), so obtained, formed white plates from alcohol, and had m. p. 63—64°, depressed by neoergostatriene but not by neoergostapentaene (Found : C, 88·6; H, 11·4. $C_{27}H_{40}$ requires C, 89·0; H, 11·0%). Iodine value, Rosenmund–Kuhnhenn method, 57; calc. for 1 double bond, 70.

Dehydrogenation of this product was attempted (i) by treatment with aluminium chloride in ice-cold carbon disulphide; (ii) by attempted removal of hydrogen bromide from the unstable crystalline bromide (formed by bromination in chloroform solution) by (a) heating at 200° in a vacuum, (b) heating in quinoline solution at 200°, (c) refluxing in pyridine solution for 12 hours, (d) heating with acetone and sodium iodide in a sealed tube at 120—125° for 16 hours; (iii) by treatment with selenium in a sealed tube at 240—250° for 5 hours; (iv) by boiling with lead peroxide in xylene suspension for 7 hours; (v) by heating with a 10% solution of sulphuric acid in acetic acid at 100° for 2 hours; (vi) by heating with platinum-black in a current of carbon dioxide at 290—295° for 40 minutes. All the products were distilled at 0·1 mm. None formed a stable picrate in alcoholic solution. In experiments (i), (iii), and (vi) a mobile oil was obtained. In the case of (vi), an unstable s.-trinitrobenzene complex was formed in alcoholic solution, but decomposition of this complex, followed by redistillation, gave a still uncrystallisable product. Experiment (ii) in every case gave crystalline products which still contained appreciable amounts of bromine and were unsaturated. Experiments (iv) and (v) gave the unchanged tetraene.

The tetraene (50 mg.) was unaffected by boiling with amyl alcohol (4 c.c.) and sodium (0·3 g.) during 1 hour.

Neoergostatriol (I).—Neoergosterol (0·5 g.), dissolved in chloroform (5 c.c.), was treated in the cold with perbenzoic acid (18 c.c. of a solution containing 3·6 g. of " active oxygen " per litre). The mixture was kept in the cold for 70 hours with addition of anhydrous sodium sulphate. The product, obtained by dilution and ether extraction, followed by removal of benzoic acid with sodium carbonate, was a yellow gum, which did not crystallise after being in contact with light petroleum for several months. It was treated with glacial acetic acid (25 c.c.) and sulphuric acid (1 drop) at 60—75° during 1 hour. The product was hydrolysed with alcoholic potassium hydroxide (10 c.c. of 10% solution); the dark gum obtained, after removal of acids, crystallised from benzene (charcoal) in white plates of *neoergostatriol* (I), m. p. 202—204°. Yield, about 30 mg. (Found : C, 78·45; H, 10·1. $C_{27}H_{44}O_3$ requires C, 78·2; H, 10·2%).

102. *Thiopyrimidazine Derivatives.*

By ROBERT ROBINSON and (MISS) M. L. TOMLINSON.

THE substances herein described have been prepared in connection with Professor R. A. Peters' researches on vitamin-B_1, and in the hope of making a contribution to that investigation by orienting studies of synthetic compounds whose composition is comparable with that of the vitamin. The striking developments in the chemistry of the flavins, due to the pioneering work of Kuhn and others, have naturally directed attention to the chemistry of the fused nuclei comprising pyrimidine and azine units. But until quite recently there was no reason to suppose that vitamin-B_1 had any connexion with this group. Peters has, however, pointed out (*Nature*, 1935, **135**, 107) that vitamin-B_1 not only has the composition of a thiohexahydrolumichrome, but can actually be converted

by simple oxidation processes into substances which exhibit the characteristic fluorescent properties of known members of the alloxazine series. We directed our attention, there-fore, to the synthesis of substances which might serve as models for the exhibition of the various characteristics of the vitamin. We have been successful in so far as the fluores-cence properties are concerned. The introduction of the thiol group appears to inhibit the exhibition of fluorescence, which, however, appears after oxidation. (These facts are private communications from Professor Peters.)

In order to effect the desired syntheses, we attempted at first the preparation of thio-alloxan; but although thiobarbituric acid (Michael, *J. pr. Chem.*, 1887, **35**, 456) could be readily nitrosated, the *thiovioluric acid* (I) produced could not be hydrolysed. We then condensed 4 : 5-diamino-2-thiouracil (II) (Traube, *Annalen*, 1903, **331**, 71) with phenyl-glyoxal (to III), with phenanthraquinone (to IV), and with *cyclo*hexane-1 : 2-dione (Riley, Morley, and Friend, J., 1932, 1878; compare Clemo and McIlwain, J., 1934, 1991, whose work appeared whilst ours was in progress). The product in the last case is considered to have the constitution (V), and on oxidation in aqueous solution the appearance of fluorescence corresponds rather closely with the behaviour of vitamin-B_1 under similar conditions. These substances are of course very different from the vitamin in other respects; they are, for example, very feebly basic, and attempts are now being made to reduce them in the hope of obtaining water-soluble bases.

Also it appears, from the available evidence, that the sulphur in the vitamin is otherwise disposed in the molecule.*

The thiopyrimidazines are infusible substances which darken from about 300° to 350°, the behaviour depending so much on the rate of heating that it was not deemed worthy of record; they all gave considerable difficulty in the analyses, leaving behind a nitrogenous residue under the usual conditions of combustion.

(I.)   (II.)   (III.)

(IV.)   (V.)
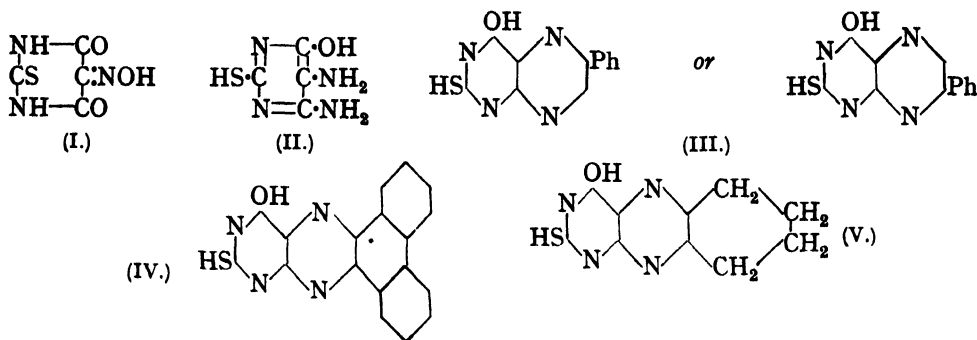
EXPERIMENTAL.

Thiovioluric Acid (I).—An aqueous solution of sodium nitrite (2·5 g.) was slowly added to a well-stirred suspension of thiobarbituric acid (5 g.) in dilute hydrochloric acid; the colourless precipitate gave place to a yellow one. This crystallised from methyl alcohol in pale yellow prisms, which fell to a deeper yellow powder as the result of loss of methyl alcohol when dried at 100° (yield, 80%; no definite m. p.) (Found : C, 28·9; H, 1·8; N, 24·6. $C_4H_3O_3N_3S$ requires C, 27·8; H, 1·7; N, 24·3%). The substance was readily soluble in aqueous alkali and showed a pronounced tendency to become green on exposure to the air, especially in contact with filter-paper and other organic matter. On reduction with a boiling aqueous solution of ammonium sulphide, 2-thiouramil was undoubtedly obtained, but it could not be isolated in a sufficiently pure state for analysis. The base separated when its solution in dilute aqueous

* The important work of Williams and his colleagues was reported in an issue of the *J. Amer. Chem. Soc.* (1935, **57**, 229; cf. Williams *et al., ibid.*, p. 536) which reached us a few days after our MS. had been submitted to the Society. Evidently the vitamin does not contain a pyrimidazine ring, but the formation of such a system on oxidation is not excluded by the new information and is even rendered more probable. The constitution proposed by the American authors is that of a derivative of an *o*-diaminopyrimidine.

ammonia was evaporated, and it exhibited a marked tendency to become deep purple in the air.

Thiobarbituric acid condensed readily in alcoholic solution with *p*-nitrosodimethylaniline. The deep green precipitate obtained was freely soluble in water, but very sparingly soluble in organic solvents. It could not be hydrolysed with the formation of thioalloxan.

p-*Toluenezothiobarbituric acid* was obtained in almost quantitative yield when a cold diazo-solution prepared from *p*-toluidine (1·1 g.), hydrochloric acid (3 c.c. of 33%), water (10 c.c.), and sodium nitrite (0·7 g.) was added to a solution of thiobarbituric acid (1·4 g.) in aqueous sodium hydroxide (3 g. in 20 c.c.). After acidification the orange-yellow mass was collected and recrystallised from much alcohol, forming orange-yellow prisms (Found : C, 50·1 ; H, 4·1. $C_{11}H_{10}O_2N_4S$ requires C, 50·4 ; H, 3·8%).

4 : 5-*Diamino-2-thiouracil* (II).—(A) This substance has been prepared by Traube (*loc. cit.*), but it does not appear to have been previously analysed (Found : C, 30·3 ; H, 3·8. $C_4H_6ON_4S$ requires C, 30·4 ; H, 3·8%).

(B) A solution of *p*-toluidine (5·3 g.) in hydrochloric acid (15 c.c., *d* 1·16) and water (50 c.c.) was diazotised by the addition of a solution of sodium nitrite (3·5 g.), and then added to a cold solution of 4-amino-2-thiouracil (8 g.) in aqueous sodium hydroxide (15 g. in 160 c.c.). The mixture was acidified and the red infusible precipitate was collected (1 part) and eventually reduced by gradual addition to a hot solution of stannous chloride (3 parts) in concentrated hydrochloric acid. The liquid was brought to ebullition and cooled ; the stannichloride that separated was collected and decomposed by trituration with concentrated aqueous ammonia, and on concentration of the filtered solution a crystalline precipitate was produced. The substance obtained appeared to be identical with Traube's diamine in respect of its solubility in aqueous ammonia and precipitation in a crystalline form on boiling ; on examination of the crystals through crossed Nicols, the extinction values of the specimens were found to be identical. The base is also characterised by the formation of a sparingly soluble hydrochloride, and by its power of reducing alkaline solutions of silver, lead salts, and Fehling's solution.

7-*Thiol-9-hydroxy-2* (or 3)-*phenylpyrimidazine* (III).—Equivalent quantities of phenyl-glyoxal and diaminothiouracil were condensed together in boiling acetic acid solution during 30 minutes. The precipitate was collected after cooling and recrystallised from acetic acid ; the yellow needles obtained (yield, 50%) lost solvent of crystallisation at 100° and fell to a yellow powder (Found : C, 56·7 ; H, 3·2 ; S, 12·0. $C_{12}H_8ON_4S$ requires C, 56·3 ; H, 3·1 ; S, 12·5%). The substance is soluble in aqueous alkalis, but its basic properties are very feebly developed.

Thiolhydroxyphenanthrapyrimidazine (IV).—This substance was prepared in a like manner from phenanthraquinone, the reaction being complete in 15 minutes (yield, 30%). The slender yellow needles that separated from hot pyridine were soluble in aqueous sodium hydroxide but insoluble in most organic solvents and in aqueous acids (Found : C, 65·1 ; H, 3·2 ; N, 16·4. $C_{18}H_{10}ON_4S$ requires C, 65·4 ; H, 3·0 ; N, 16·9%).

11-*Thiol-13-hydroxy-3 : 4 : 5 : 6-tetrahydrobenzpyrimidazine* (V).—The substance usually termed *cyclo*hexanedione must be almost pure *cyclo*hexenonol, for it has none of the properties associated with the true α-diketones. It is colourless, devoid of sharp odour (the odour is more phenolic in character and resembles that of hydroxymethylene*cyclo*hexanone, or even that of salicylaldehyde), immediately soluble in alkalis, and gives an intense brownish-green ferric reaction. It was originally described as a crystalline solid, m. p. 38—40°, by Wallach (*Annalen,* 1924, **437**, 174), but Riley, Morley, and Friend (*loc. cit.*) obtained it only as an oil. It is therefore of interest that the product which we employed, and which was prepared by the method of the latter authors, crystallised completely and had m. p. 38—40°.

The condensation with an equivalent of diaminothiouracil in boiling acetic acid solution occupied 1 hour and the solid material that separated on cooling was recrystallised from acetic acid (yield, 25%), forming pale yellow needles. A better method consisted in heating the mixed reactants without solvent (oil-bath at 130—140°) for 15 minutes ; the mass effervesced and then solidified. On trituration with aqueous ammonia a salt was obtained, and this crystallised from water in fine yellowish needles which lost solvent of crystallisation on drying at 100°. After decomposition by means of dilute hydrochloric acid, the *substance* crystallised from much hot water or from acetic acid in slender yellow needles (yield, 55%) ; the product from water was anhydrous (Found : C, 50·8 ; H, 4·4 ; S, 12·8. $C_{10}H_{10}ON_4S$ requires C, 51·3 ; H, 4·3 ; S, 13·7%). A further examination is being made by Professor Peters.

Thioltrihydroxybispyrimidazine.—Condensation of diaminothiouracil and alloxan was effected in the usual manner in acetic acid solution ; the product was very sparingly soluble in organic solvents, but could be purified by crystallisation of its pyridine salt from aqueous pyridine.

The yellow plates were decomposed by means of dilute hydrochloric acid, and the resulting yellow powder analysed (Found : C, 32·2; H, 2·8. $C_8H_4O_3N_6S,2H_2O$ requires C, 32·0; H, 2·7%). This material was readily soluble in aqueous ammonia and other alkaline solutions.

Condensation of diaminothiouracil with isatin affords a deep red, insoluble substance which has not been purified. It dissolves in alkalis to deep red solutions, but no crystalline derivative has so far been encountered.

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103. *Conversion of 3-Nitro-4-methylphenylarsonic Acid into 3-Amino-4-carboxyphenylarsonic Acid by Intramolecular Dismutation, and the Action of Hydrobromic Acid on* m-*Arsanilic Acid and 3-Amino-4-carboxyphenylarsonic Acid.*

By ARCHIBALD H. C. P. GILLIESON, WILLIAM O. KERMACK, and WALTER T. SPRAGG.

PREUSS and BINZ (*Z. angew. Chem.*, 1900, **16**, 385) state that anthranilic acid is formed in 20% yield when o-nitrotoluene (2 parts) and sodium hydroxide (2 parts) in water (1 part) are refluxed for five hours (cf. also D.R.-P. 114839), and D.R.-P. 138188 claims that 2-nitro-p-toluenesulphonic acid (I; R =- SO_3H) yields 3-amino-4-carboxybenzenesulphonic acid (II; R = SO_3H) in good yield by treatment with 30% sodium hydroxide solution. It appeared of interest to ascertain with what yield, if any, the dismutation takes place in the case of 3-nitro-4-methylphenyl-arsonic acid and -stibonic acid (I; R = AsO_3H_2 and SbO_3H_2 respectively). The latter acid, when treated with aqueous caustic soda of various concentrations, gave none of the desired 3-amino-4-carboxyphenylstibonic acid, but from

3-nitro-4-methylphenylarsonic acid a yield of 10—15% of 3-amino-4-carboxyphenylarsonic acid (II; R = AsO_3H_2) was obtained by refluxing with 30% aqueous sodium hydroxide for 8 hours. The product was identical (isoelectric point, crystalline appearance, fluorescence and spectra of derived azo-dyes) with 3-amino-4-carboxyphenylarsonic acid prepared by the method of Cohen, King, and Strangeways (J., 1931, 3250), the chief difference being in the colour, which, however, showed considerable variation, due to traces of impurity, even when the same method was used. In the absence of any m. p. below 400° identification by means of mixed m. p.'s could not be effected. Both specimens, when heated with hydrobromic acid (*d* 1·58) (cf. Phillips, J., 1930, 2400; Schuster, *Compt. rend.*, 1932, **195**, 611) in a sealed tube at 160° for 8 hours, were converted into *p*-bromoaniline, identified as its acetyl derivative.

In order to obtain information as to the mechanism of this unexpected reaction, similar treatment with fuming hydrobromic acid at 160° was applied to aniline, m-bromoaniline, anthranilic acid, and m-arsanilic acid. The first two substances are recovered unchanged, the third yielded aniline, and from m-arsanilic acid an oil was obtained which gave *p*-bromoacetanilide on acetylation. Since under the above conditions decarboxylation of anthranilic acid takes place, it presumably occurs also with 3-amino-4-carboxyphenylarsonic acid. The mechanism of the replacement of the arsono-group by bromine has been discussed by Prat (*Compt. rend.*, 1934, **198**, 583).

The above results are most easily explained on the assumption that the hydrobromic acid causes fission of the arsono-group as arsenic acid, and that the aniline thus produced is brominated by bromine set free by the conversion of the arsenic from the quinque- to the ter-valent condition. In accordance with this view, after aniline hydrobromide had been heated with hydrobromic acid and arsenic acid in a sealed tube at 160°, *p*-bromo-

aniline hydrobromide (identified as *p*-bromoacetanilide) separated on cooling, but none was obtained when the arsenic acid was omitted or replaced by arsenious oxide. Presumably the bromination occurs on those molecules of aniline temporarily existing as free base, as the aniline ions would be expected to undergo *m*-bromination.

The replacement of the arsono-group by bromine has been advocated by Phillips and by Schuster (*locc. cit.*) as a useful method for identifying arsonic acids. Though our conditions are more drastic than theirs, the abnormal results obtained with *m*-arsanilic acid and 3-amino-4-carboxyphenylarsonic acid indicate the need for caution in the application of the method.

EXPERIMENTAL.

Dismutation of 3-*Nitro*-4-*methylphenylarsonic Acid.*—The acid (26 g.) was refluxed for 9 hours with 130 c.c. of 30% aqueous sodium hydroxide and the dark brown solution was then diluted to 200 c.c., filtered, and treated with hydrochloric acid until it was acid to litmus but still alkaline to Congo-red; a white gelatinous precipitate (mainly unchanged acid) separated in small quantity. The filtrate was further acidified until it gave a bluish-purple colour with Congored; a light brown, tarry precipitate was formed and filtered off. The filtrate was evaporated to 50 c.c., cooled, and, after removal of sodium chloride, boiled with charcoal and filtered. The solution still gave a bluish-purple colour with Congo-red, and sodium carbonate solution was added until the colour was reddish-purple; on standing over-night, a buff precipitate separated. This was purified by the method of Cohen, King, and Strangeways (*loc. cit.*). Yield, 3·1 g. (Found : As, 29·0. Calc. for $C_7H_8O_5NAs$: As, 28·7%).

Treatment of 3-*Amino*-4-*carboxyphenylarsonic Acid with Hydrobromic Acid.*—The arsonic acid (0·5 g., prepared by the above method) was heated in a sealed tube for 8 hours at 160° with hydrobromic acid (5 c.c., d 1·58). The crystals of hydrobromide which separated on cooling were collected and the base was liberated with sodium hydroxide and extracted and dried in ether; a further quantity was obtained from the hydrobromic acid mother-liquor. The oily base was heated with acetic anhydride on the water-bath for 30 minutes. The acetyl derivative obtained (0·19 g.) crystallised from ligroin in white needles, m. p. 164—165° alone or mixed with authentic *p*-bromoacetanilide (m. p. 167°). Mixed m. p.'s with *m*-bromoacetanilide (m. p. 84°) and 2 : 5-dibromoacetanilide (m. p. 172°) gave quite definite depressions.

104. *Thionaphthenopyrazoles.*

By W. J. BARRY and E. W. McCLELLAND.

3-HYDROXYTHIONAPHTHENS with an acyl group in the 2-position (I) react with hydrazines in acid media to give pyrazoles; *e.g.*, 3-hydroxy-2-acetyl-1-thionaphthen reacts with phenylhydrazine and with *p*-bromophenylhydrazine to give the *thionaphthenopyrazoles* (II : R = Me, R' = Ph; R = Me, R' = *p*-C_6H_4Br). Similarily, 3-hydroxy-2-benzoyl-1-thionaphthen (I; R = Ph) reacts with phenylhydrazine to give the *diphenylthionaphtheno-pyrazole* (II; R = R' = Ph). The formation of the pyrazoles takes place by way of the corresponding hydrazones, since they are also obtained from the appropriate hydrazones by heating with alcoholic sulphuric acid. 3-Hydroxy-2-acetyl-1-thionaphthen condenses with hydrazine hydrochloride in alcohol to give a small amount of the pyrazole (II; R = Me, R' = H) and a red substance of high melting point which is presumably a *bis-compound* (VI or VII). When the condensation is effected in acetic acid, the pyrazole alone is obtained.

Oxidation of the sulphur to the sulphone condition in many cyclic systems appears to restrain the tendency to enolisation (compare McClelland, J., 1929, 1588; Cohen and Smiles, J., 1930, 406; Levi and Smiles, J., 1931, 520; McClelland and D'Silva, J., 1932,

227). Therefore it was considered that the dioxides formed by oxidation of the thionaphthenopyrazoles might not be identical with those obtained directly from the thionaphthen dioxides (IV). Oxidation of the thionaphthenopyrazoles gave, however, dioxides identical with those obtained from the corresponding thionaphthen dioxides and the appropriate hydrazines by the method of Cohen and Smiles (*loc. cit.*).
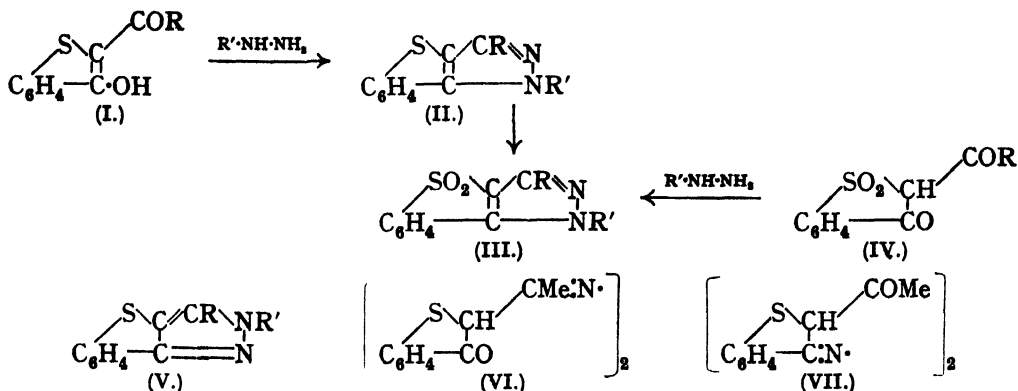
It is evident that the condensation of a phenylhydrazine with a 2-acyl hydroxythionaphthen (I) may yield two isomeric pyrazoles (II and V), but the formation of isomerides has not been detected. Since the bivalent sulphur in the thionaphthen system favours enolisation at the 3-position, the thionaphthenopyrazoles have presumably the structure (II), although the alternative structure (V) cannot be excluded. In order to eliminate this alternative, attempts were made to degrade the thionaphthenopyrazoles but without success. It was found, however, that the corresponding dioxides were susceptible to alkaline reduction, sulphur being eliminated during the process. Thus reduction of the pyrazole dioxide (III; $R = Me$, $R' = H$) by sodium amalgam gave 5(3)-phenyl-3(5)-methylpyrazole (Sjollema, *Annalen*, 1894, **279**, 248; Auwers and Stuhlmann, *Ber.*, 1926, **59**, 1048). The pyrazole dioxide (III; $R = Me$, $R' = Ph$) reacted with sodium in alcohol to give a small amount of 1 : 5-diphenyl-3-methylpyrazoline (Auwer and Mauss, *Ber.*, 1926, **59**, 611), thus confirming the structure (II) assigned to the thionaphthenopyrazoles. The main product of the reaction is, however, a *substance* (A), m. p. 122—124°. The analysis of this material corresponds to a diphenylmethylpyrazole. It is neither 1 : 5-diphenyl-3-methylpyrazole nor 1 : 3-diphenyl-5-methylpyrazole (compare Auwers and Mauss, *loc. cit.*; Drumm, *Proc. Roy. Irish Acad.*, 1930, **40**, B, 106). The latter might be expected to result from the pyrazole dioxide if the thionaphthenopyrazole had the structure (V). The material (A) forms a *mononitroso*-compound, and also a *monobromo*-compound which is not identical with 4-bromo-1 : 5-diphenyl-3-methylpyrazole (Drumm, *loc. cit.*).

It being assumed that a new cyclic system has not been formed, consideration of these properties and those recorded in the experimental section suggests that (A) may be 1 : 5-diphenyl-4-methylpyrazole, formed by migration of the methyl group during reduction of the thionaphthenopyrazole dioxide (III; $R = Me$, $R' = Ph$). The possibility of an intramolecular rearrangement with the formation of a non-pyrazole cyclic system cannot be excluded.

EXPERIMENTAL.

1-Phenyl-3-methyl-4 : 5-thionaphthenopyrazole (II; $R = CH_3$, $R' = Ph$).—A solution of 3-hydroxy-2-acetyl-1-thionaphthen (10 g.) and phenylhydrazine hydrochloride (10 g.) in alcohol (80 c.c.) was refluxed for 3 hours. The *pyrazole* (10 g.), which separated on cooling, crystallised from alcohol in colourless needles, m. p. 120° [Found : C, 72·7; H, 4·4 (Schoeller); N, 10·7. $C_{16}H_{12}N_2S$ requires C, 72·7; H, 4·6; N, 10·6%]. It was also obtained by refluxing 3-hydroxy-2-acetyl-1-thionaphthen and phenylhydrazine in acetic acid for 4 hours.

Oxidation.—The pyrazole (10 g.) in acetic acid (100 c.c.) containing hydrogen peroxide (30 c.c., 100 vol.) was heated at 100° for 1 hour. The material, obtained by dilution, after

purification gave no depression when mixed with 1-phenyl-3-methyl-4 : 5-thionaphtheno-pyrazole S-dioxide.*

1-p-*Bromophenyl-3-methyl-4 : 5-thionaphthenopyrazole* (II; R = CH₃, R' = *p*-C₆H₄Br).— 3-Hydroxy-2-acetyl-1-thionaphthen (5 g.) and *p*-bromophenylhydrazine (5 g.) in alcohol (50 c.c.) were refluxed for 2 hours. Sulphuric acid (1 c.c.) was added, and the refluxing continued for 5 minutes. The *product*, after being washed successively with alkali, acid, and water, crystallised from alcohol in colourless needles, m. p. 159° (Found : C, 55·8; H, 3·7; Br, 23·6. C₁₆H₁₁N₂BrS requires C, 56·0; H, 3·2; Br, 23·3%). 3-*Hydroxy-2-acetyl-1-thionaphthen-p-bromophenylhydrazone*, obtained by heating the components in alcohol for 1¼ hours, crystallised from alcohol in brown plates or yellow needles, m. p. 160—161° (Found : C, 52·8; H, 3·7. C₁₆H₁₃ON₂BrS requires C, 53·2; H, 3·6%); it gave the pyrazole when heated with alcoholic sulphuric acid.

1-p-*Bromophenyl-3-methyl-4 : 5-thionaphthenopyrazole Dioxide* (III; R = CH₃, R' = *p*-C₆H₄Br)—The above pyrazole (1 g.) in acetic acid (20 c.c.) and hydrogen peroxide (5 c.c., 100 vol.) was heated at 100° for 1 hour. The *product*, which crystallised from acetic acid in colourless plates, m. p. 207°, was identical with that obtained from 3-hydroxy-2-acetyl-1-thionaphthen 1 : 1-dioxide (1 g.) and *p*-bromophenylhydrazine (1 g.) by refluxing in alcohol containing sulphuric acid (Found : C, 51·2; H, 3·3. C₁₆H₁₁O₂N₂BrS requires C, 51·2; H, 2·95%).

1 : 3-*Diphenyl-4 : 5-thionaphthenopyrazole* (II; R = R' = Ph).—A solution of 3-hydroxy-2-benzoyl-1-thionaphthen (10 g.) and phenylhydrazine (10 g.) in alcohol (300 c.c.) was refluxed for 10 hours. Sulphuric acid (5 c.c.) was added, and the mixture heated for 2 hours. The material which separated on cooling crystallised from alcohol in colourless needles, m. p. 171° [Found : C, 77·4; H, 4·3 (Schoeller); N, 8·5. C₂₁H₁₄N₂S requires C, 77·3; H, 4·3; N, 8·6%]. The *pyrazole* (1 g.) in acetic acid (20 c.c.) and hydrogen peroxide (5 c.c., 100 vol.), heated at 100° for 1¼ hours, gave on dilution a material, which after purification from acetic acid had m. p. 225° alone or mixed with 1 : 3-diphenyl-4 : 5-thionaphthenopyrazole S-dioxide.*

Condensation of Hydrazine with 3-*Hydroxy-2-acetyl-1-thionaphthen.*—A solution of the thionaphthen (5 g.) in alcohol (50 c.c.) and hydrazine hydrochloride (5 g.) was refluxed for 1 hour. The material (*bis-compound*) which separated during the reaction was filtered off. It crystallised from aniline in red needles, m. p. 305° (Found : C, 62·9; H, 4·4; N, 7·7. C₂₀H₁₆O₂N₂S₂ requires C, 63·1; H, 4·2; N, 7·4%). This compound was insoluble in acid and alkali and was unaffected by heating with alcoholic sulphuric acid. The filtrate, after removal of the bis-compound, was neutralised with aqueous sodium hydroxide; 3-*methyl-4 : 5-thio-naphthenopyrazole* (II; R = CH₃, R' = H) slowly separated. It crystallised from alcohol in colourless needles, m. p. 185° (Found : C, 63·2; H, 4·2. C₁₀H₈N₂S requires C, 63·8; H, 4·3%). The pyrazole alone was obtained when 3-hydroxy-2-acetyl-1-thionaphthen (10 g.) and hydrazine hydrochloride (10 g.) in acetic acid (100 c.c.) were refluxed for 4 hours; the pyrazole hydro-chloride which separated on cooling was dissolved in water, and the solution neutralised. The pyrazole is soluble in acid and alkali and forms a silver salt. The *pyrazole dioxide*, obtained in the usual way, crystallised from acetic acid in colourless needles, m. p. 244—246° (Found : N, 13·0. C₁₀H₈O₂N₂S requires N, 12·7%).

Reduction of the Thionaphthenopyrazole Dioxides.—(i) Sodium amalgam (20 g. of 5%) was added to a solution of 3-methyl-4 : 5-thionaphthenopyrazole dioxide (1 g.) in 2N-sodium hydroxide (10 c.c.). The mixture was warmed, and kept over-night. The solution was poured into an excess of 2N-sulphuric acid, boiled till free from sulphur dioxide, and neutralised. Extraction with ether gave a material, which after crystallisation from water and finally from ligroin had m. p. 123° and gave no depression with 5(3)-phenyl-3(5)-methylpyrazole.

(ii) A solution of 1-phenyl-3-methyl-4 : 5-thionaphthenopyrazole (5 g.) in alcohol (100 c.c.) was refluxed for 3 hours, during which sodium (5 g.) was added portionwise. The solid which separated was filtered off and washed with alcohol. (This material gave Smiles' sulphinic acid test.) It was dissolved in water, and the aqueous solution acidified, boiled till no more sulphur dioxide was evolved, and cooled. The *product* (A) crystallised from alcohol in colourless needles, m. p. 122—124° (Found : C, 82·3; H, 5·5; N, 12·0. C₁₆H₁₄N₂ requires C, 82·0; H, 6·0; N, 12·0%). The filtrate, obtained above, was evaporated to dryness, and the residue treated with water and extracted with ether. The product from the ethereal solution, crystallised from alcohol, melted at 114° alone or at 114—116° with 1 : 5-diphenyl-3-methylpyrazoline and gave an identical colour reaction with sodium nitrite in sulphuric acid.

Properties and Reactions of (A).—The substance (A) does not give Knorr's pyrazoline test

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* The authors are indebted to Professor Smiles for specimens of these dioxides.

and is insoluble in aqueous alkali. It is basic, forming easily hydrolysable salts with mineral acids and an unstable methiodide, m. p. (*ca.*) 135°. It was recovered unchanged after heating with concentrated hydrochloric acid at 180° for 6 hours and was not susceptible to reducing agents. Bromine in chloroform was added to a solution of (A) in chloroform until decoloration ceased. The solvent was removed, and the residue washed with aqueous sodium carbonate (10%). The product crystallised from acetic acid in colourless needles, m. p. 142—143° [Found : Br, 24·9 (Schoeller). $C_{16}H_{13}N_2Br$ requires Br, 25·5%]. (A) (0·5 g.) was dissolved in sulphuric acid (10 c.c. of 60%) with warming. The solution was cooled, and sodium nitrite (0·2 g.) added. After standing over-night, the mixture was diluted with water and partly neutralised. The solid which separated crystallised from acetic acid in green needles, m. p. 202—203° [Found : N, 16·5 (Schoeller). $C_{16}H_{13}ON_3$ requires N, 16·0%].

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105. *Derivatives of* bicyclo[0 : 3 : 3]*Octane.*

By J. C. BARDHAN and S. K. BANERJI.

THE chemistry of *bicyclo*[0 : 3 : 3]octane derivatives has been recently brought into prominence by the work of Wieland and his collaborators (*Z. physiol. Chem.*, 1924, **134**, 276; 1930, **191**, 69) on monocyclic fission products of bile acids. The parent member of this group was, however, first prepared by Schroeter (*Annalen*, 1922, **426**, 1) by a series of reactions the exact nature of which is little understood. More recently, Ruzicka, Borges de Almeida, and Brack (*Helv. Chim. Acta*, 1934, **17**, 183) and Linstead and co-workers (J., 1934, 935) have made a comprehensive study of the synthetical problem.

We have developed a new method of attack, the results of which are now recorded in view of Cook and Linstead's work (*loc. cit.*, p. 958).

It seemed to us probable that an acid of the structure (I) should on distillation in a vacuum furnish a *bicyclo*octane derivative (II), since Wieland and Vocke (*Z. physiol. Chem.*, 1928, **177**, 68) had shown that the analogously constituted tetrabasic acid (III) under the above conditions passed smoothly into the pyro-acid (IV).
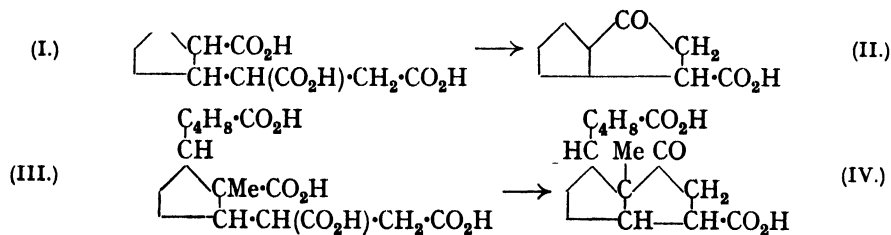
A convenient method for the preparation of the acid (I) appeared to be the condensation of ethyl Δ¹-*cyclo*pentenecarboxylate with ethyl sodiocyanoacetate and treatment of the resulting sodio-derivative with ethyl bromoacetate. Repeating the condensation of ethyl sodiocyanoacetate with ethyl Δ¹-*cyclo*pentenecarboxylate according to Sircar (J., 1927,

(Compare Thorpe, J., 1900, **77**, 928.)
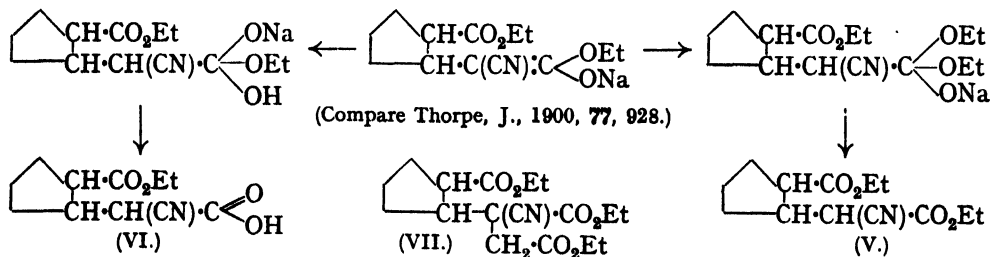
1255; compare also Cook and Linstead, *loc. cit.*, p. 959), we obtained a considerably smaller yield of the cyano-ester (V) than that reported by them. The chief product of the con-

densàtion was the ethyl hydrogen ester (VI, not mentioned by those workers) the yield of which was a maximum after 12 hours' heating. The crude condensation product was treated directly with ethyl bromoacetate, and a good yield of the cyano-ester (VII) obtained. This ester on hydrolysis with sulphuric acid furnished the tribasic *acid* (I), distillation of which in a vacuum, however, did not give a satisfactory yield of the keto-acid (II).

On distillation under reduced pressure the ethyl hydrogen ester (VI) passed smoothly into the cyano-ester (VIII), hydrolysis of which with concentrated hydrochloric acid gave *trans*-1-carboxy*cyclo*pentane-2-acetic acid, m. p. 66° (Linstead and Meade, *loc. cit.*, p. 946), also obtained from the ester (V) by hydrolysis with 65% sulphuric acid.

The acid (I) was converted by the alcohol vapour method into its triethyl ester (IX), which reacted with " molecular " sodium, giving a good yield of *ethyl* bicyclo[0 : 3 : 3]*octan*-1-*one*-2 : 3-*dicarboxylate* (X). This was readily converted by dilute hydrochloric acid into *bicyclo*[0 : 3 : 3]octan-1-one-3-carboxylic acid, which was characterised by the formation of the *semicarbazone*. The keto-acid regenerated therefrom could not be obtained in a solid state, probably owing to the formation of a mixture of *cis*- and *trans*- modifications. We wish to reserve this point and the conversion of the keto-acid into *bicyclo*[0 : 3 : 3]octane for a future communication.
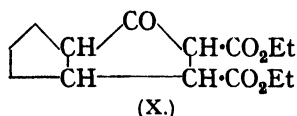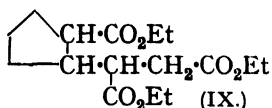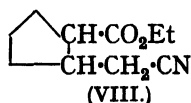
$$\text{(VIII.)} \qquad \text{(IX.)} \qquad \text{(X.)}$$

EXPERIMENTAL.

Condensation of Ethyl Δ^1-cyclo*Pentenecarboxylate with Ethyl Sodiocyanoacetate.*—Ethyl Δ^1-*cyclo*pentenecarboxylate was prepared by the action of phosphoryl chloride on ethyl *cyclo*-pentan-1-ol-1-carboxylate in dry benzene. 52 G. of the hydroxy-ester yielded 37 g. of the pure unsaturated ester, boiling constantly at 70°/4 mm. (bath 80—85°). The ester on hydrolysis gave Δ^1-*cyclo*pentenecarboxylic acid, m. p. 121°.

The following experiments on the addition of ethyl sodiocyanoacetate to ethyl Δ^1-*cyclo*-pentenecarboxylate were made with a view to determine the exact conditions under which a maximum yield of the ethyl hydrogen ester (VI) could be obtained. The quantities employed were : 16·95 g. of ethyl cyanoacetate, 21·5 g. of the unsaturated ester, and 3·45 g. of sodium, dissolved in 56 c.c. of absolute alcohol. When the heating was finished, the condensation product was poured into water and separated into a neutral and an acid fraction in the usual way. The neutral fraction was finally distilled under reduced pressure to remove the unchanged ester.

Hours of heating	1	6	12	24
Ethyl ester (V.), g.	13	5	2	2·3
Ethyl hydrogen ester (VI), g.	9	21	24	24

Ethyl α-cyano-1-carbethoxy*cyclo*pentane-2-acetate (V) was obtained as a colourless oil, b. p. 162°/5 mm. (Found : C, 61·6; H, 7·7. Calc. : C, 61·7; H, 7·5%). Ethyl α-cyano-1-carbethoxy*cyclo*pentane-2-acetic acid (VI), which formed the main constituent of the acid fraction, decomposed on distillation under reduced pressure, giving 1-*carbethoxy*cyclo*pentane*-2-*acetonitrile* (VIII), a colourless oil, b. p. 128°/4 mm., 265°/757 mm. (Found : C, 66·3; H, 8·5. $C_{10}H_{15}O_2N$ requires C, 66·3; H, 8·3%).

The crude acid fraction (21 g.) containing the acid (VI) was heated with absolute alcohol (75 c.c.) and concentrated sulphuric acid (4·5 c.c.) at 110° in a current of alcohol vapour for 5 hours. The ester (V) obtained had b. p. 165°/6 mm. (yield, 21 g.). A portion of it, on hydrolysis with 65% sulphuric acid for 6 hours, gave a good yield of *trans*-1-carboxy*cyclo*pentane-2-acetic acid, m. p. 66°. We prefer this method, as the hydrochloric acid method used by previous workers requires a much longer time (30 hours) for completion.

*Action of Ethyl Bromoacetate on the Sodio-derivative of Ethyl α-Cyano-1-carbethoxy*cyclo-*pentane-2-acetate.*—The condensation of ethyl Δ^1-*cyclo*pentenecarboxylate with ethyl sodio-cyanoacetate was brought about as described in the third experiment (12 hours' heating) above. The product was cooled in ice, treated with ethyl bromoacetate (17 c.c.) and, the vigour of the reaction having abated, heated on a steam-bath until neutral. The whole was then cooled and poured into a large volume of water, and the heavy oil was collected in ether, washed with water, dried, recovered, and fractionated under reduced pressure, *ethyl* α-*cyano*-1-*carbethoxy*-

cyclo*pentane-2-succinate* (VII) being obtained as a colourless, somewhat viscous oil (40 g.), b. p. 207°/5 mm. (Found : C, 60·5; H, 7·5. $C_{17}H_{28}O_6N$ requires C, 60·2; H, 7·4%).

The ester (VII) (60 g.) was heated with concentrated sulphuric acid (65 c.c.) and water (80 c.c.) under reflux for 15 hours, the alcohol formed being allowed to escape. On cooling, 1-*carboxy*cyclo*pentane-2-succinic acid* (I) separated, for the most part in a crystalline state; it was washed with as little water as possible and recrystallised from hot water, separating in well-formed prisms, m. p. 202° [Found : C, 52·2; H, 6·2; equiv., by titration, 77·0. $C_{10}H_{14}O_6$ (tribasic) requires C, 52·2; H, 6·1%; equiv., 76·7]. It is sparingly soluble in cold water and almost insoluble in ether, benzene, and light petroleum.

Ethyl 1-*carbethoxy*cyclo*pentane-2-succinate* (IX) was obtained in an almost quantitative yield from the acid (I) by the alcohol vapour method : in a typical experiment the acid (26 g.), alcohol (50 c.c.), and sulphuric acid (5 c.c.) gave 32 g. of the ester, b. p. 172°/4 mm. (Found : C, 61·4; H, 8·4. $C_{16}H_{26}O_6$ requires C, 61·1; H, 8·3%). The ester readily dissolved when boiled for a short time with concentrated hydrochloric acid; the solution, on cooling, deposited the acid, m. p. 202°, in a pure state.

Sodium-condensation of Ethyl 1-*Carbethoxy*cyclo*pentane-2-succinate.*—The ester (10 g.) was dissolved in benzene (25 c.c.) and heated with " molecular " sodium (1·5 g.) on the steam-bath for 3 hours. The product was cooled in ice and treated with dilute sulphuric acid. The benzene layer was removed, washed successively with water, sodium carbonate solution, and water, dried, and distilled, *ethyl* bicyclo[0 : 3 : 3]*octan-1-one-2* : 3-*dicarboxylate* (X) being obtained as a colourless oil (6 g.), b. p. 166°/6 mm. (Found : C, 62·8; H, 7·6. $C_{14}H_{20}O_5$ requires C, 62·7; H, 7·5%). Its alcoholic solution gives a reddish-violet coloration with aqueous ferric chloride.

The keto-ester (X) (10 g.) was heated under reflux with hydrochloric acid (30 c.c.; d 1·19) and water (80 c.c.) for 3 hours. From the cooled solution, saturated with ammonium sulphate, ether extracted an oil, which was heated with semicarbazide hydrochloride (5 g.), sodium acetate (6 g.), and water (10 c.c.) on the steam-bath, enough alcohol being then added to make a clear solution. After a short time, the *semicarbazone* separated as a sandy powder; purified from absolute alcohol, it had m. p. 210° (Found : C, 53·1; H, 6·7; N, 18·7. $C_{10}H_{15}O_3N_3$ requires C, 53·3; H, 6·7; N, 18·7%). The bicyclo[0 : 3 : 3]*octan-1-one-3-carboxylic acid* regenerated from the semicarbazone by means of dilute hydrochloric acid in the usual way was a gum, which partly crystallised in a vacuum desiccator after several weeks. Owing to the small amount available, it could not be further investigated.

106. *Terpene Compounds. Part I. Preliminary Synthetical Investig-ations in the Cadinene Group.*

By J. C. BARDHAN and S. K. BANERJI.

THE structure of the dicyclic sesquiterpenes of the cadinene group has been definitely established by Ruzicka and his collaborators (*Helv. Chim. Acta*, 1921, **4**, 505; 1922, **5**, 357, 369; 1923, **6**, 86) by conversion into the fundamental naphthalene hydrocarbon cadalene and by analytical methods. Apart from the work of Ruzicka and Capato (*ibid.*, 1925, **8**, 289), no attempt appears to have been made hitherto to confirm the structural details respecting the orientation of the double bonds by rational synthesis.

Preliminary experiments which we have carried out in this direction, with the object of synthesising dihydrocadinol (I) and dihydrocadinene (II) (compare, however, Ruzicka and Stoll, *ibid.*, 1923, **6**, 94), are now described.

The starting point was ethyl Δ³-tetrahydro-*p*-toluate, the preparation of large quantities of which from 4-methylcyclohexanone presented little difficulty. This was condensed with ethyl sodiocyanoacetate, and the resulting sodio-derivative allowed to react with ethyl β-chloropropionate, a good yield *of ethyl* . 1-*carbethoxy-4-methyl*cyclohexane-2-α-

(*α-cyanoglutarate*) (III) being obtained.   This on hydrolysis with sulphuric acid gave the expected tricarboxylic acid (as IV).   The corresponding *ester* (IV) was cyclised with granu-

$$\begin{array}{cc}
& \text{CH}_2 \quad \text{CHMe} \\
\text{(I.)} & \text{H}_2\text{C} \quad \text{CH} \quad \text{CH}_2 \\
& \text{MeHC} \quad \text{CH} \quad \text{CH}_2 \\
& \text{CH}_2 \quad \text{CPr}^\beta\text{·OH}
\end{array}
\qquad
\begin{array}{cc}
\text{CH}_2 \quad \text{CHMe} & \\
\text{H}_2\text{C} \quad \text{CH} \quad \text{CH}_2 & \text{(II.)} \\
\text{MeHC} \quad \text{CH} \quad \text{CH} & \\
\text{CH}_2 \quad \text{CPr}^\beta &
\end{array}$$
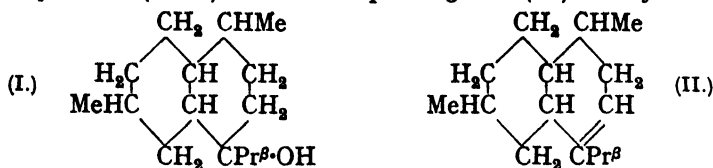
lated sodium in dry benzene, and the product on hydrolysis gave a crystalline substance (V) ·which showed all the properties of a ketonic acid.

$$\begin{array}{c}
\text{H}_2 \\
\text{H}_2 \quad \text{CH·CO}_2\text{Et} \\
\text{MeH} \quad \text{CH·C(CN)(CO}_2\text{Et)·[CH}_2]_2\text{·CO}_2\text{Et} \\
\text{H}_2 \quad \text{(III.)}
\end{array}
\qquad
\begin{array}{c}
\text{H}_2 \\
\text{H}_2 \quad \text{CH·CO}_2\text{Et} \\
\text{MeH} \quad \text{CH·CH(CO}_2\text{Et)·[CH}_2]_2\text{·CO}_2\text{Et} \\
\text{H}_2 \quad \text{(IV.)}
\end{array}$$
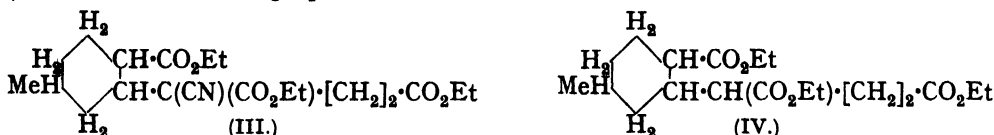
The *keto-ester* (as V), treated with methylmagnesium iodide, gave a neutral product; this was probably derived from (VI), since on dehydrogenation with selenium it furnished a good yield of cadalene, identified by its boiling point and by its picrate, m. p. 115°.

$$\begin{array}{cc}
& \text{CH}_2 \quad \text{CO} \\
\text{(V.)} & \text{H}_2\text{C} \quad \text{CH} \quad \text{CH}_2 \\
& \text{MeHC} \quad \text{CH} \quad \text{CH}_2 \\
& \text{CH}_2 \quad \text{CH·CO}_2\text{H}
\end{array}
\qquad
\begin{array}{cc}
\text{CH}_2 \quad \text{CMe·OH} & \\
\text{H}_2\text{C} \quad \text{CH} \quad \text{CH}_2 & \text{(VI.)} \\
\text{MeHC} \quad \text{CH} \quad \text{CH}_2 & \\
\text{CH}_2 \quad \text{CH·CMe}_2\text{·OH} &
\end{array}$$
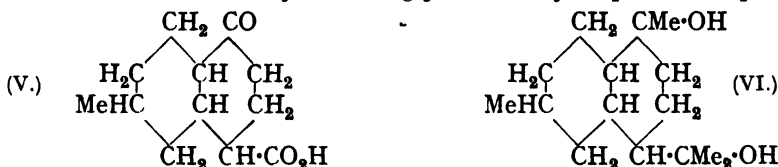
The yield of the acid fraction in the above condensation was very small.   We are trying to improve the yield of the product (VII), from which by a simple series of transformations we hope to prepare the ketone (VIII).

At the outset of this research we made some preliminary experiments on the formation of *bicyclo*nonane derivatives from ethyl Δ^3-tetrahydro-*p*-toluate.   The product of the interaction of ethyl sodiocyanoacetate and ethyl Δ^3-tetrahydro-*p*-toluate readily reacted with ethyl bromoacetate to give (IX), which on hydrolysis gave a gummy acid.   It is somewhat

$$\begin{array}{c}
\text{CH}_2 \quad \text{CMe·OH} \\
\text{H}_2\text{C} \quad \text{CH} \quad \text{CH}_2 \\
\text{MeHC} \quad \text{CH} \quad \text{CH}_2 \\
\text{CH}_2 \quad \text{CH·CO}_2\text{H} \\
\text{(VII.)}
\end{array}
\qquad
\begin{array}{c}
\text{CH}_2 \quad \text{CHMe} \\
\text{H}_2\text{C} \quad \text{CH} \quad \text{CH}_2 \\
\text{MeHC} \quad \text{CH} \quad \text{CH}_2 \\
\text{CH}_2 \quad \text{CO} \\
\text{(VIII.)}
\end{array}
\qquad
\begin{array}{c}
\text{H}_2 \\
\text{H}_2 \quad \text{CH·CO}_2\text{Et} \\
\text{MeH} \quad \text{CH·C(CN)(CO}_2\text{Et)·CH}_2\text{·CO}_2\text{Et} \\
\text{H}_2 \\
\text{(IX.)}
\end{array}$$
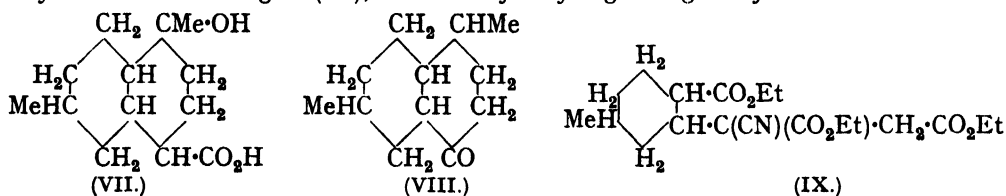
remarkable that tricarboxylic acids of this series show no tendency to solidify, especially in view of the fact that the corresponding tricarboxylic acid from ethyl Δ^1-*cyclo*pentene-carboxylate can be readily obtained in the solid state (compare Bardhan and Banerji, preceding paper).   The *ester* (X) on condensation with granulated sodium gave the dicyclic *keto-ester* (XI), which on hydrolysis furnished a keto-acid (XII), characterised by its *semicarbazone*.

$$\begin{array}{c}
\text{H}_2 \\
\text{H}_2 \quad \text{CH·CO}_2\text{Et} \\
\text{MeH} \quad \text{CH·CH·CO}_2\text{Et} \\
\text{H}_2 \quad \text{CH}_2\text{·CO}_2\text{Et} \\
\text{(X.)}
\end{array}
\qquad
\begin{array}{c}
\text{CH}_2 \quad \text{CO} \\
\text{H}_2\text{C} \quad \text{CH} \quad \text{CH·CO}_2\text{Et} \\
\text{MeHC} \quad \text{CH——CH·CO}_2\text{Et} \\
\text{CH}_2 \\
\text{(XI.)}
\end{array}
\qquad
\begin{array}{c}
\text{CH}_2 \quad \text{CO} \\
\text{H}_2\text{C} \quad \text{CH} \quad \text{CH}_2 \\
\text{MeHC} \quad \text{CH——CH·CO}_2\text{H} \\
\text{CH}_2 \\
\text{(XII.)}
\end{array}$$
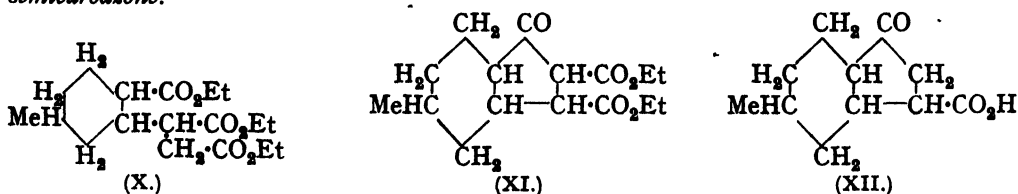
Experimental.

Δ^3-Tetrahydro-*p*-toluic acid was first prepared by Perkin and Pickles (J., 1905, **87**, 645) from *p*-toluic acid (they named it Δ^1-tetrahydro-*p*-toluic acid).   For the preparation of the

large quantities required for the present research the following method gave excellent results. 4-Methyl*cyclo*hexanone (100 g.) was shaken with a solution of sodium bisulphite (200 g.) in water (250 c.c.), and the mixture was then cooled in ice and gradually treated with a solution of potassium cyanide (75 g.) in water (150 c.c.). After some time the cyanohydrin was collected in ether, washed with water, and dried (anhydrous sodium sulphate), and the solvent removed with the addition of 2—3 drops of concentrated sulphuric acid. The crude cyanohydrin was refluxed with 5—6 vols. of concentrated hydrochloric acid (d 1·19) for 5 hours on the steam-bath, and the hydroxy-acid extracted with ether (yield, 100 g.; m. p. 130°). The hydroxy-acid (50 g.) was cautiously mixed with phosphorus pentachloride (135 g.) and heated on the steam-bath until the latter had gone into solution (10—12 hours). The product was well cooled, poured into ice-cold absolute alcohol (200 c.c.), and left over-night. Dilution in much water precipitated a heavy oil, which was separated and hydrolysed with an excess of 20% potassium hydroxide solution. The last traces of alcohol were removed on the water-bath, the brown solution cooled, filtered, and acidified with hydrochloric acid, and the solid product collected (yield, 33 g.; m. p. 132°).

Ethyl Δ³-tetrahydro-*p*-toluate was prepared by refluxing a mixture of the acid (126 g.), absolute alcohol (350 c.c.), and concentrated sulphuric acid (50 c.c.) for 8 hours (yield, 125 g.; b. p. 95°/5 mm.) (compare Perkin and Pickles, *loc. cit.*).

Ethyl 1-*Carbethoxy*-4-*methyl*cyclohexane-2-α-(α-*cyanoglutarate*) (III).—A solution of sodium (11·5 g.) in absolute alcohol (188 c.c.) was cooled in ice and gradually mixed with ethyl cyano-acetate (57 g.). After ¼ hour ethyl Δ³-tetrahydro-*p*-toluate (84 g.) was added, and the mixture refluxed on the steam-bath for 24 hours. The brownish crystalline mass, consisting of the sodio-derivative of the condensation product, was cooled in ice and treated with ethyl β-chloropropion-ate (69 g.), the mixture being finally heated for 6 hours. After cooling, the product was poured into water, and the oil extracted with ether, washed, dried, and fractionated under diminished pressure. *Ethyl* 1-*carbethoxy*-4-*methyl*cyclohexane-2-α-(α-*cyanoglutarate*) had b. p. 198°/2 mm., $d_4^{20·2°}$ 1·08347, $n_D^{20·2°}$ 1·46340, $[R_L]_D$ 97·01 (calc., 97·14) (Found : C, 62·4; H, 8·3. $C_{20}H_{31}O_6N$ requires C, 62·7; H, 8·1%). Yield, 118 g.

Ethyl 1-*Carbethoxy*-4-*methyl*cyclohexane-2-α-*glutarate* (IV).—A solution of the above cyano-ester (118 g.) in concentrated sulphuric acid (120 c.c.) was diluted with water (120 c.c.) and refluxed for 40 hours, the condenser being removed from time to time to allow the alcohol produced to escape. After cooling, the mixture was diluted with water, and the semi-solid mass extracted with ether. The gummy acid (80 g.) obtained was converted by the alcohol vapour method [in a typical experiment : acid, 115 g.; absolute alcohol, 230 c.c.; concentrated sulphuric acid, 23 c.c.; 6 l. of alcohol vaporised; (7 hours)] into *ethyl* 1-*carbethoxy*-4-*methyl*cyclohexane-2-α-*glutarate*, a colourless limpid oil, b. p. 168°/2 mm., $d_4^{30·6°}$ 1·0326, $n_D^{30·6°}$ 1·45542, $[R_L]_D$ 93·61 (calc., 92·7) (Found : C, 64·6; H, 9·0. $C_{19}H_{32}O_6$ requires C, 64·0; H, 9·0%) (yield from the above quantities, 112 g.).

1-*Keto*-6-*methyldecalin*-4-*carboxylic Acid* (V).—A mixture of the foregoing ester (26·7 g.) and granulated sodium (3·45 g.) in dry benzene (54 c.c.) was refluxed for 1 hour to start the reaction. The heating was discontinued until the vigour of the reaction abated and was then continued for 3—4 hours. After cooling, the product was treated with cold dilute sulphuric acid, and the benzene layer was washed with aqueous sodium carbonate and with water, dried, and evaporated. The residue gave a violet coloration with ferric chloride, but could not be distilled without decomposition. The crude product (13 g.) was refluxed with excess of dilute sulphuric acid (20%) for 8 hours, the cooled solution saturated with ammonium sulphate and repeatedly extracted with ether, and the extract washed with water, dried, and distilled; as the residue of acid contained an appreciable amount of the ester, it was further hydrolysed with 10% alcoholic potash, and the product isolated in the usual way. The keto-acid was thus obtained as a semi-solid crystalline mass, which was spread on a porous plate and purified by several crystallisations from aqueous alcohol (charcoal). 1-*Keto*-6-*methyldecalin*-4-*carboxylic acid* formed colourless prisms, m. p. 191° (previous softening), sparingly soluble in ether (Found : C, 67·9; H, 8·5. $C_{12}H_{18}O_3$ requires C, 68·6; H, 8·6%). The *semicarbazone* separated from methyl alcohol in colourless needles, m. p. 216° (Found : C, 58·7; H, 7·9. $C_{13}H_{21}O_3N_3$ requires C, 58·4; H, 7·9%), and when warmed with dilute hydrochloric acid re-generated the keto-acid, m. p. 191°.

The *ethyl* ester, prepared by refluxing a solution of the keto-acid (105 g.) in absolute alcohol (350 c.c.), with the addition of absolute alcohol (35 c.c.) saturated at 0° with hydrogen chloride, formed a colourless, somewhat viscous oil (65 g.), b. p. 142°/3 mm., $d_4^{22°}$ 1·04887, $n_D^{20°}$ 1·47985, $[R_L]_D$ 64·4 (calc., 64·1) (Found : C, 70·7; H, 9·3. $C_{14}H_{22}O_3$ requires C, 70·6; H, 9·2%); its

semicarbazone, crystallised from ethyl alcohol, had m. p. 192° (Found : C, 61·7; H, 8·9. $C_{15}H_{25}O_2N_3$ requires C, 61·0; H, 8·5%), and the *oxime* separated from dilute alcohol in colourless silky needles, m. p. 160° (Found : C, 66·7; H, 9·3. $C_{14}H_{23}O_3N$ requires C, 66·4; H, 9·1%).

Action of Methylmagnesium Iodide on Ethyl 1-Keto-6-methyldecalin-4-carboxylate.— The ester (10 g.), diluted with dry ether (10 c.c.), was slowly added to a solution of methyl-magnesium iodide (prepared from magnesium, 3·6 g., dry ether, 100 c.c., and methyl iodide, 11 c.c.) cooled in ice-water. After standing for 12 hours at the ordinary temperature, the product was decomposed with ice and dilute hydrochloric acid. The solution was extracted ten times with ether and the extract was washed with water, dried, and evaporated. The brown residue was boiled with a solution of potassium hydroxide (10 g.) in water (10 c.c.) and alcohol (90 c.c.) for 1 hour, the alcohol removed as completely as possible, and the residue diluted with water and repeatedly extracted with ether (extract A) (yield, 4 g.). The alkaline solution was acidified with hydrochloric acid and again extracted with ether (extract B). Extract A on removal of the solvent gave a neutral oil having a terpene-like odour. No product of definite composition could be obtained from it, but when it was heated with selenium it gave a good yield of cadalene, b. p. 130—159°/10 mm. (picrate, m. p. and mixed m. p. 115°). The regenerated cadalene was a colourless oil, b. p. 149°/10 mm. (Found : C, 91·2; H, 9·2. Calc. : C, 90·9; H, 9·1%).

Extract (B) consisted of acidic products, the investigation of which is not yet complete.

Ethyl 1-Carbethoxy-4-methylcyclohexane-2-α-cyanosuccinate (IX) [with R. G. CHATTERJEE and N. N. CHATTERJEE].—The condensation of ethyl tetrahydro-*p*-toluate with ethyl sodio-cyanoacetate was carried out as described above, and the resulting sodio-derivative heated with ethyl bromoacetate for 6 hours. The ester (IX) is a colourless viscous liquid, b. p. 215°/7 mm., $d_4^{30·1°}$ 1·095225, $n_D^{30·1°}$ 1·467172, $[R_L]_D$ 92·75 (calc., 92·52) (Found : C, 61·5; H, 8·1. $C_{19}H_{29}O_6N$ requires C, 62·1; H, 7·9%). Yield, 50 g.

Ethyl 1-Carbethoxy-4-methylcyclohexane-2-succinate (X).—Hydrolysis of the above cyano-ester with 8% sulphuric acid yielded a gummy acid which, esterified by the alcohol vapour method, gave the *triethyl* ester (X), b. p. 165—167°/2 mm. (Found : C, 63·1; H, 9·0. $C_{18}H_{30}O_6$ requires C, 63·15; H, 8·8%).

Ethyl 7-Methyl-[0 : 3 : 4-bicyclo]nonan-2-one-3 : 4-dicarboxylate (XI).—The above ester (10 g.) was heated with granulated sodium (1·4 g.) and benzene (25 c.c.) until the whole of the sodium disappeared (2 hours). The *ester* (XI) was obtained as a colourless oil (5 g.), b. p. 186°/7 mm. (Found : C, 64·9; H, 8·1. $C_{16}H_{24}O_5$ requires C, 64·8; H, 8·1%). Its alcoholic solution gave a violet coloration with ferric chloride. Hydrolysis of the ester furnished a keto-acid (XII), which would not solidify but readily gave a *semicarbazone*, minute prisms, m. p. 221—222° (decomp.), after recrystallisation from alcohol (Found : N, 16·4. $C_{12}H_{19}O_5N_3$ requires N, 16·6%). The regenerated keto-acid was a gum which partly solidified and probably consisted of a mixture of stereoisomerides.

Ethyl 3 : 7-Dimethyl-[0 : 3 : 4-bicyclo]nonan-2-one-3 : 4-dicarboxylate.—The ester (X) (9 g.) was cyclised with sodium (1·4 g.) in benzene, the product cooled in ice and gradually treated with an excess of methyl iodide (10 c.c.), and the whole warmed until neutral. The mixture was treated with cold water and the benzene layer was separated, dried, and distilled, *ethyl 3 : 7-dimethyl-[0 : 3 : 4-bicyclo]nonan-2-one-3 : 4-dicarboxylate* being obtained as a colourless oil (4 g.), b. p. 175°/8 mm. (Found : C, 66·1; H, 8·3. $C_{17}H_{26}O_5$ requires C, 65·9; H, 8·3%). It did not give a coloration with alcoholic ferric chloride.

Ethyl 1-Carbethoxy-4-methylcyclohexane-2-(α-cyano-α'-methylsuccinate).—This *ester*, obtained in good yield by treating the product of the condensation of ethyl Δ³-tetrahydro-*p*-toluate and ethyl sodiocyanoacetate with ethyl α-bromopropionate, was an almost colourless oil, b. p. 208°/8 mm. (Found : C, 62·9; H, 7·9. $C_{20}H_{31}O_6N$ requires C, 62·9; H, 8·1%).

Ethyl 1-Carbethoxy-4-methylcyclohexane-2-α'-methylsuccinate.—The foregoing cyano-ester on hydrolysis with sulphuric acid gave the expected tricarboxylic acid as a gum. The corre-sponding *ester* was readily obtained as a colourless oil, b. p. 175°/7 mm. (Found : C, 64·3; H, 8·8. $C_{19}H_{32}O_6$ requires C, 64·0; H, 8·8%).

107. *The Dipole Moments of* p-*Cymene ; 2- and* 3-*Halogeno-*p-*cymenes, Carvacrol, and Thymol ;* p-*Ethyltoluene ;* p-*tert.-Butyltoluene, 1 : 3-Dimethyl-5-tert.-butylbenzene, tert.-Butylbenzene and its* p-*Nitro-derivative.*

By Catherine G. Le Fèvre, Raymond J. W. Le Fèvre, and (in part) Kathleen W. Robertson.

Previously (*Nature*, 1933, **131**, 655; *Chem. and Ind.*, 1933, **52**, 505) the following *a priori* conditions were regarded as sufficient to cause a 1 : 4-disubstituted benzene derivative to exhibit substitution phenomena at variance with expectations based on current theories alone : (*a*) that a marked difference in volume between the two groups should exist, (*b*) that the inductive effects of the competing groups should roughly compensate one another or be not very dissimilar, and (*c*) that electromerisations should not be unequally initiated or facilitated by the two radicals concerned.

A suitable compound for examination being a 1 : 4-dialkylbenzene, *p*-cymene was chosen (J., 1933, 680) rather than *p*-ethyl- or *p-tert.*-butyl-toluene because, although condition (*b*) most probably held for all three hydrocarbons, it was not certain that conditions (*a*) and (*c*) applied respectively to the second and the third. The following four sections deal with points of interest which arose when making this selection.

Section I. The Dipole Moment of p-*Cymene.*—In the preceding communications (*locc. cit.*), aromatic substitution, with particular reference to *p*-cymene, has been viewed in the manner commonly adopted in this country, *viz.*, that electrophilic (kationoid) reagents are effective by virtue of a constitutional affinity for electrons, and therefore attack most fruitfully those nuclear carbon atoms at which the necessary high electron densities can be developed; and that the electron-supply mechanisms, by which such alterations of electron distribution are achieved at the various points, can be, in the first analysis, subdivided into *permanent* and *temporary* polarisation effects within the molecule undergoing substitution.

In the absence of external activating influences (such as the fields of reagent molecules), a molecule will exhibit only the former effect, which can therefore be assessed by a determination of the dipole moment of the substance concerned.

The application to the case of cymene is easy, for if in this compound all electronic displacements arising from the methyl group are neutralised by those from the *iso*propyl radical, the resultant dipole moment should be zero * and the 2 : 6- and 3 : 5-positions equally activated. Whether or not this is the case cannot be decided owing particularly to the uncertainty of the dielectric constant data, reproduced in the following table. In

Dielectric Constant and Molecular Polarisation of p-*Cymene from Data in the Literature.*

Temp.	$d_4^{\cdot}$.	ϵ.	P, c.c.	Temp.	$d_4^{\cdot}$.	ϵ.	P, c.c.
15·58°	0·86004 [1]	2·231 [1]	45·31	18·00°	0·85875 [6]	2·43 [3]	50·37
17·24	0·85913 [1]	2·230 [1]	45·36			2·25 [4]	45·89
17·00	0·85949 [6]	2·26 [3]	46·11	176·5	0·7248 [5]	2·27 [3]	54·99

[1] Landolt and Jahn, *Z. physikal. Chem.*, 1892, **10**, 289.   [3] Grimm and Patrick, *J. Amer. Chem. Soc.*, 1923, **45**, 2794.   [3] Mathews, *J. Physical Chem.*, 1905, **9**, 641.   [4] Nernst, *Z. physikal. Chem.*, 1894, **14**, 622.   [5] Schiff, *Annalen*, 1883, **220**, 94.   [6] Present work.

col. 4 are shown the total polarisations, calculable by the usual Clausius–Mosotti formula from the appropriate values in cols. 2 and 3. These, combined with the calculated molecular refractivity (for Na_D light) of cymene would correspond to moments ranging from 0 to 1 Debye unit.

In view of these disagreements, we made the series of redeterminations recorded below. *Measurements.*—The dielectric constants were measured by the resonance method described

* The possibility of polarisation *within* the Pr^β group is small in view of the zero moment recorded for 1 : 4-diethylbenzene (Weissberger and Sängewald, *Physikal. Z.*, 1929, **30**, 792).

by J. W. Smith (*Proc. Roy. Soc.*, 1932, *A*, **136**, 251), modified in the one detail that a high tension voltage of 220 v. can be substituted satisfactorily for the 900 v. specified in this reference. We wish to acknowledge our indebtedness to Dr. J. W. Smith for help and advice in setting up the apparatus. A cell of the Sayce–Briscoe type, silvered by the recipe of Sugden—whose statements regarding the permanency of the silver film produced by this and other methods we confirm—was used in preference to other types. The experimental procedure followed is fully described in Smith's paper, where the methods of calculation are illustrated.

The refractive indexes were determined with a Pulfrich refractometer, a Phillips " Neron " lamp affording a convenient source of yellow light.

For the density determinations the Perkin modification of Sprengel's pyknometer (J., 1884, **45**, 421) was found to give better results than the usual Ostwald–Sprengel type, which could not be wiped so easily prior to weighing. The pyknometers were of *ca.* 10 c.c. capacity; the final densities should be accurate to 0·00001.

Materials.—The benzene and carbon tetrachloride were purified as described by Le Fèvre and Smith (J., 1932, 2239). The purity of the *p*-cymene used would appear to require comment. Von Auwers (*Annalen*, 1919, **419**, 114) has pointed out that certain physical properties (notably the refractive index) of this hydrocarbon vary according to the mode of preparation, so we therefore had to eliminate impurities which might themselves have a moment. Probable contaminants of this nature are (in synthetic products) *m*-cymene and (in commercial supplies from spruce turpentine) certain compounds (? terpenic hydrocarbons) which sometimes cause a slight optical activity. *m*-Cymene must have constituted a large part of the sample of " *p*-cymene " prepared by the Friedel–Crafts method examined by von Auwers (cf. Kelbe, *Annalen*, 1881, **210**, 25), and is probably never entirely absent from specimens obtained by the action of phosphoric oxide on camphor (cf. Armstrong and Miller, *Ber.*, 1883, **16**, 2259; these, in addition, are exceedingly difficult to free from the last traces of phosphorus compounds). Owing to their close b. p.'s, separation of the *m*- and the *p*-isomeride by fractional distillation is impossible.

We therefore first used material prepared from crystalline thymol by the following sequence :
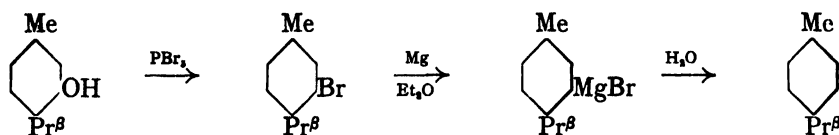
This gave the pure hydrocarbon quite satisfactorily; but later we found that identical results were obtained by purifying a commercial specimen as described subsequently.

(a) *Preparation of Cymene from Thymol.*—Thymol (100 g.) was heated under reflux for 2 hrs. with phosphorus pentabromide (70 g.); water was then added, the mixture steam-distilled, the distillate extracted with ether, and the extract washed, dried (sodium sulphate), and distilled, 30 g. of 3-bromocymene, b. p. 130°/35 mm., being obtained. This compound (48 g.), dry ether (500 c.c.), and magnesium (6 g.) were refluxed together until solution was complete. Water in excess was then added slowly, followed by dilute sulphuric acid. The ethereal layer was separated, dried (calcium chloride), and distilled. The crude *p*-cymene obtained was once redistilled (column); b. p. 177—178°/760 mm. (yield, 22 g.).

(b) *Purification of Technical Cymene.*—Several litres (obtained from Messrs. Hopkin and Williams) were refluxed over powdered sulphur for 2 days, shaken with successive quantities of concentrated sulphuric acid until the latter was no longer coloured, then twice treated with a little chlorosulphonic acid, and subsequently (after a rough washing with water) with potassium permanganate solution, followed by dilute aqueous sodium hydroxide. Finally, the material was dried (sodium sulphate) and fractionated through a Dufton column; b. p. 177—177·5°/760 mm.; $d_4^{25°}$ 0·85341, $n_D^{25°}$ 1·48878.

Results.—The symbols used in the tables below have the usual significance, subscripts 1 and 2 referring to solute and solvent in cases where this is possible.

Molecular Polarisation of Liquid Cymene.

Temp.	$d_4^{t°}$.	ϵ.	P, c.c.	Temp.	$d_4^{t°}$.	ϵ.	P, c.c.
4°	0·87013	2·2653	45·68	40°	0·83970	2·1992	45·57
18	0·85875	2·2451	45·77	45	0·83588	2·1950	45·67
20·9	0·85643	2·2409	45·78	50	0·83205	2·1828	45·54
25	0·85341	2·2322	45·72	60	0·82439	2·1684	45·56

Molecular Polarisation of Cymene in Benzene Solution.

Temperature 25°.

$10^4 f_1$.	$M_1 f_1 + M_2 f_2$	ϵ.	d.	$P_1 f_1 + P_2 f_2$	$P_2 f_2$.	$P_1 f_1$.	P_1.
0	78	2·2725	0·87380	26·585	26·585	—	—
11,457	78·6416	2·2717	0·87351	26·802	26·280	0·522	45·57
18,188	79·0186	2·2713	0·87337	26·929	26·101	0·828	45·52
21,001	79·1761	2·2710	0·87335	26·979	26·027	0·952	45·32
24,011	79·3447	2·2708	0·87330	27·035	25·947	1·087	45·28
89,922	83·0357	2·2660	0·87320	28·221	24·194	4·027	44·78
195,086	88·9248	2·2583	0·87213	30·129	21·399	8·730	44·75

Whence P_1 extrapolated to $f_1 = 0$ is 45·62 c.c.

Temperature 45°.

$10^4 f_1$.	$M_1 f_1 + M_2 f_2$	ϵ.	d.	$P_1 f_1 + P_2 f_2$	$P_2 f_2$.	$P_1 f_1$.	P_1.
0	78	2·2333	0·85210	26·664	26·664	—	—
11,457	78·6416	2·2327	0·85199	26·882	26·359	0·523	45·62
18,188	79·0186	2·2325	0·85198	27·000	26·179	0·829	45·57
24,011	79·3447	2·2317	0·85170	27·116	26·024	1·092	45·47
89,922	83·0357	2·2270	0·84788	28·428	24·266	4·072	45·28
195,086	88·9248	2·2193	0·84840	30·290	21·462	8·828	45·25

Whence P_1 extrapolated to $f_1 = 0$ is 45·79 c.c.

Molecular Polarisation of Cymene in Carbon Tetrachloride.

Temperature 0°.

$10^4 f_1$.	$M_1 f_1 + M_2 f_2$	ϵ.	d.	$P_1 f_1 + P_2 f_2$	$P_2 f_2$.	$P_1 f_1$.	P_1.
0	154	2·2748	1·63170	28·116	28·116	—	—
22,432	153·5514	2·2744	1·60598	28·507	27·485	1·0212	45·52
55,486	152·8903	2·2714	1·56491	29·081	26·556	2·5246	45·50
80,878	152·3824	2·2732	1·53818	29·517	25·842	3·6750	45·44
121,662	151·5668	2·2735	1·49489	30·214	24·695	5·5187	45·36

Whence P_1 extrapolated to $f_1 = 0$ is 45·61 c.c.

Temperature 20°.

$10^4 f_1$.	$M_1 f_1 + M_2 f_2$	ϵ.	d.	$P_1 f_1 + P_2 f_2$	$P_2 f_2$.	$P_1 f_1$.	P_1.
0	154	2·2345	1·59402	28·1368	28·1368	—	—
22,432	153·5514	2·2350	1·56957	28·529	27·506	1·0234	45·62
55,486	152·8903	2·2371	1·53386	29·103	26·576	2·5269	45·54
80,878	152·3824	2·2385	1·50731	29·540	25·861	3·6792	45·49
121,662	151·5668	2·2402	1·46577	30·244	24·714	5·5307	45·46

Whence P_1 extrapolated to $f_1 = 0$ is 45·62 c.c.

The Dipole Moment of p-*Cymene.*—From the above results the total polarisation of *p*-cymene is 45·66 ± 0·04 c.c. According to accepted theories, this is the sum of the electronic, atomic, and orientation polarisations. The first of these equals the molecular refractivity for light of infinite wave-length, $[M_L]_\infty$, which is calculated as 43·6 c.c. from the following data (Landolt–Börnstein–Roth, 4th Edn., p. 1039) : M_α, 44·87 ; M_D, 45·18 ; M_β, 45·96 ; M_γ, 46·62 c.c. The atomic polarisation cannot be stated with certainty. If, following Debye (" Polar Molecules," 1929, p. 43), $P_E + P_A$ is assumed equal to the molecular refractivity for the D line, then $P_O - 45\cdot66 - 45\cdot18 = 0\cdot48$ c.c., and $\mu = 0\cdot01273(0\cdot48 \times 298)^{1/2} = 0\cdot15 \times 10^{-18}$ e.s.u.

A probably more accurate result can be obtained if the atomic polarisation of cymene be taken as equal to that of *p*-xylene (*i.e.*, 2 c.c. ; Smyth, *J. Amer. Chem. Soc.*, 1929, **51**, 2051 ; *J. Chem. Physics*, 1933, **1**, 247) rather than to 15% of P_E ; that such an estimate is evidently of the right order, follows from the fact that, although the atomic polarisation increases roughly with the number of atomic nuclei in a given series of molecules, yet the change from benzene to *p*-xylene is only 0·5 c.c. Thus $P_O = 45\cdot66 - (43\cdot6 + 2) = ca.$ 0, and μ is also zero. A similar conclusion must be drawn from the temperature invariance of the polarisation.

Confirmation of this value can be obtained from a comparison of the Kerr constant of cymene with that of benzene, because in such molecules where the electric moments lie along the axes of maximum polarisability, a parallelism is generally observed between the magnitudes of their Kerr constants (B) and their moments (cf. Briegleb and Wolf, *Fortsch. Chem.*, 1931, **21**, Part 3). Now B = (term due to anisotropy) + (dipole term)

(Debye, "Handbuch der Radiologie," **6**, Leipzig, 1925) and *p*-cymene, which has almost certainly * a greater anisotropy term than benzene, has a Kerr constant which is only slightly greater ($B = 15\cdot7$ instead of $12\cdot1$). The contrast with, *c.g.*, toluene is marked—even so small a moment as that found for this hydrocarbon ($\mu = 0\cdot4 \times 10^{-18}$ e.s.u.) corresponds to a Kerr constant ($B = 24\cdot3$) nearly double that of benzene. By inference, therefore, *p*-cymene must have a vanishingly small moment.

Section II. The Dipole Moments of 2- *and* 3-*Halogeno*-p-*cymenes, Carvacrol, and Thymol.*—The extent to which activation of the various nuclear carbon atoms by temporary polarisation effects can become operative during aromatic substitution will obviously vary with the reaction and other factors, and always be difficult to estimate. Cymene, however, offers a simplification in that not more than two pairs of equal positions are available for substitution, and information regarding only their *relative* activation is desired. An attempt was therefore made to deduce this from observations of the dipole moments of 2- and 3-chloro-, -bromo-, and -hydroxy-*p*-cymenes.

In these isomeric compounds the substituents are regarded as corresponding, in their polarising actions on the attached hydrocarbon structures, to the effective parts of the reagent molecules engaged in attacking the 2 : 6- and the 3 : 5-positions of cymene at some comparable stage, *before* substitution is completed *but* when propinquity has caused the polarisability of the hydrocarbon towards the particular point of address to become developed. Since the unsubstituted cymene molecule is non-polar (Section I), any observable differences of dipole moment between the 2- and 3-isomerides must be held to imply that during electrophilic reagent action either the 2- or the 3-nuclear position is likely to become more polarised, and hence achieve a greater activation, depending on which of each isomeric pair has the greater moment.

Materials.—2-Chlorocymene (for preparation, see J., 1933, 983), b. p. 216—217°/761 mm., $d_4^{17°} \ 1\cdot0208$, $n_D^{17°} \ 1\cdot51776$, whence $[R_L]_D \ 50\cdot0$ (Calc., 49·6). 3-Chlorocymene (for preparation, see J., 1934, 848), b. p. 120—122°/20 mm., $d_4^{18°} \ 1\cdot01799$, $n_D^{18°} \ 1\cdot51796$, whence $[R_L]_D \ 50\cdot15$. 2-Bromocymene (from direct halogenation of the hydrocarbon, see J., 1933, 981), b. p. 229—230°/765 mm., $d_4^{18°} \ 1\cdot26889$, $n_D^{18°} \ 1\cdot54162$, whence $[R_L]_D \ 52\cdot8$ (Calc., 52·5). 3-Bromocymene (from thymol, see J., 1934, 848), b. p. 235°/760 mm., $d_4^{18°} \ 1\cdot26865$, $n_D^{18°} \ 1\cdot54275$, whence $[R_L]_D$ 52·9. The thymol used had m. p. 50° and was not further purified.

Carvacrol was available only as commercial products obtained from an *Origanum* oil from Asia Minor; the most probable impurity would appear to be thymol, the separation of which from carvacrol is exceedingly difficult owing to close similarities in physical properties. The material used in the following determinations was prepared as follows : the commercial, completely alkali-soluble phenol, b. p. 230—240°/760 mm., was kept at $-$ 10° for a day, a certain quantity of thymol crystallising, and the liquor was distilled through a long column, only the condensate of b. p. 237—237·5°/760 mm. being collected. That the substance still contained impurities was indicated by the fact that when a mixture of it (15 g.) with ethyl alcohol (250 c.c.), sodium hydroxide (8 g.), and *p*-nitrobenzoyl chloride (17 g.) was heated under reflux for an hour, the *p*-nitrobenzoyl ester afforded by the usual procedure solidified only after standing in a vacuum for some weeks, and then required crystallisation from alcohol before the m. p. reached the constant value, 50°. Hydrolysis of this purified ester afforded carvacrol which solidified in a freezing mixture (Jahns, *Ber.*, 1882, **15**, 815, gives m. p. 0·5—1·0°) and gave a phenylurethane as radiating bunches of needles, m. p. 132—133° (Goldschmidt, *Ber.*, 1893, **26**, 2086, gives 134—135°, and Gildemeister, *Arch. Pharm.*, 1895, **233**, 188, m. p. 140°). Similar treatment of the carvacrol used in the following work gave a phenylurethane, m. p. *ca.* 110°, not raised by several recrystallisations from various solvents. ·A rough mixed m. p. curve for the urethanes of carvacrol and thymol showed that this specimen would contain 20—30% of the thymol derivative.

Measurements.—These are given in the following tables, being summarised in the last.

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* Cymene cannot be regarded as less anisotropic than benzene. Experiments on the scattering of light show that benzene and toluene have practically the same anisotropy terms, the former possibly being slightly the smaller; for *p*-xylene, however, a definitely larger term is indicated (Ramakrishna Rao, *Indian J. Physics*, 1927, **2**, 61; Ramachandra Rao, *ibid.*, 1928, **3**, 21). The actual case of *p*-cymene does not appear to have been investigated.

Molecular Polarisation of 2-Chlorocymene in Benzene Solution.

$10^6 f_1$.	$M_1 f_1 + M_2 f_2$.	ϵ.	$d_4^{25°}$.	$P_1 f_1 + P_2 f_2$.	$P_2 f_2$.	$P_1 f_1$.	P_1.
0	78	2·2725	0·87380	26·5850	26·5850	—	—
8,432·1	78·7631	2·3041	0·87593	27·2447	26·3608	0·8839	104·82
22,181·5	80·0075	2·3548	0·87924	28·3094	25·9953	2·3141	104·33
32,803·6	80·9687	2·3939	0·88180	29·1292	25·7129	3·4163	104·14
34,993·0	81·1669	2·4022	0·88230	29·3024	25·6547	3·6477	104·24

Whence extrapolated P_1 for $f_1 = 0$ is 105·3 c.c.

Molecular Polarisation of 3-Chlorocymene in Benzene Solution.

1,842·4	78·1667	2·2785	0·87385	26·7298	26·5360	0·1938	105·19
5,168·3	78·4677	2·2906	0·87483	26·9799	26·4476	0·5323	102·99
11,245·7	79·0177	2·3096	0·87588	27·4147	26·2860	1·1286	100·36
17,063·3	79·5442	2·3301	0·87783	27·8347	26·1314	1·7034	99·83

Whence extrapolated P_1 for $f_1 = 0$ is 106·0 c.c.

Molecular Polarisation of 2-Bromocymene in Benzene Solution.

1,574·2	78·0802	2·2828	0·87498	26·7277	26·5445	0·1832	116·38
3,111·6	78·4199	2·2865	0·87618	26·8625	26·5036	0·3590	115·36
5,059·6	78·6826	2·2946	0·87721	27·0385	26·4518	0·5867	115·96
8,373·5	79·1297	2·3098	0·88025	27·3196	26·3637	0·9559	114·16

Whence extrapolated P_1 for $f_1 = 0$ is 116·6 c.c.

Molecular Polarisation of 3-Bromocymene in Benzene Solution.

2,383·0	78·3215	2·2826	0·87551	26·7913	26·5229	0·2684	112·63
5,179·0	78·6988	2·2943	0·87754	27·0291	26·4486	0·5805	112·09
6,246·2	78·8428	2·2985	0·87831	27·1170	26·4202	0·6968	111·56
6,991·0	78·9431	2·3017	0·87884	27·1821	26·4004	0·7817	111·82

Whence extrapolated P_1 for $f_1 = 0$ is 113·1 c.c.

Molecular Polarisation of Carvacrol in Benzene Solution.*

13,258	78·9548	2·3169	0·87586	27·4994	26·2325	1·2669	95·56
14,037	79·0107	2·3193	0·87597	27·5496	26·2118	1·3378	95·30
18,668	79·3442	2·3344	0·87671	27·8623	25·0887	1·7736	95·01
28,902	80·0809	2·3680	0·87831	28·5554	25·8167	2·7387	94·76

Whence extrapolated P_1 for $f_1 = 0$ is 95·7 c.c.

Molecular Polarisation of Thymol in Benzene Solution.*

13,256·3	78·9544	2·3158	0·87585	27·4837	26·2326	1·2511	94·75
16,096·6	79·1589	2·3275	0·87631	27·7108	26·1571	1·5532	96·49
21,143·0	79·5222	2·3417	0·87711	28·0175	26·0229	1·9946	94·34
30,006·5	80·1646	2·3705	0·87850	28·6146	25·7857	2·8289	94·28

Whence extrapolated P_1 for $f_1 = 0$ is 95·4 c.c.

Refractivity Data for Carvacrol and Thymol in Benzene Solution at 25°.*

$10^6 f_1$.	n.	n^2.	$R_1 f_1 + R_2 f_2$.	$R_2 f_2$.	$R_1 f_1$.	R_1.
0	1·49733	2·24200	26·1357	26·1357	—	—
			Carvacrol.			
13,258	1·49773	2·24320	26·4114	25·7891	0·6223	46·94
14,037	1·49775	2·24326	26·4283	25·7688	0·6595	46·98
18,668	1·49789	2·24367	26·5230	25·6478	0·8752	46·88
			Thymol.			
21,143·0	1·49791	2·24372	26·5711	25·5831	0·9880	46·73
30,006·5	1·49815	2·24444	26·7543	25·3499	1·4044	46·80

* With (Miss) K. W. Robertson.

Summary of Results.

Substance.	Total polarisation, c.c.	Distortion polarisation, c.c.	P_0, c.c.	$\mu \times 10^{18}$.
2-Chlorocymene	105·3	50·0	55·3	1·64
3-Chlorocymene	106·0	50·15	56·85	1·66
2-Bromocymene	116·6	52·8	63·8	1·76
3-Bromocymene	113·1	52·9	60·2	1·71
Carvacrol............................	95·7	47	48·7	1·54
Thymol	95·4	46·8	48·6	1·54

developed in aromatic nuclei where the lower alkyl radicals are concerned, although, at the same time, the *possibility* that such effects might arise if a sufficiently strong polar influence were to approach the nucleus is illustrated by their obvious presence in, *e.g.*, the homologous alkyl halides, where a greater juxtaposition of the polar halogen and the polarisable alkyl occurs.

A point of interest arising out of the above measurements is that the moments of the chloro-, bromo-, and to a less extent the hydroxy-cymenes are not identical with those of the appropriate monosubstituted aryl compounds, but differ from them in the directions of the corresponding aliphatic analogues. This is easily explicable when the moment of a given aryl halide is regarded as the vector sum of the following three factors : (1) the unknown natural moment of a C–Cl link, (2) the additional moment caused by the inductive $(-I)$ effect of the halogen on the electronic distribution in the aromatic nucleus, and (3) the further superimposed moment originating by the (mesomerising) action of the benzenoid system on the polarisable halogen atom. In proceeding from, say, a phenyl to a cymyl halide, the relative significances of these three effects are changed. In the latter, the presence of the methyl and the *iso*propyl group (these radicals having, in the unsubstituted hydrocarbon, equal $+ I$ inductive actions opposed at 180°) will operate to increase the electron density in the nucleus and thus make it more polarisable; this, in the halogen derivatives of cymene, will allow the additional moment (2) to become more developed and/or cause a diminution of the mesomeric polarisation contribution, with the effect that the resultant molecular moments will numerically approach the figures for typically aliphatic halogeno-compounds. It is also noteworthy that these cymyl halides have moments of the same order as the *p*-tolyl halides. It therefore follows that the reversed moments in the benzene halides due to the $+ M$ effects of the halogen atoms must be, in magnitude, not far removed from those caused by the (inductive, $+ I$) action of the methyl group, a relationship which causes $\mu_{p\text{-}Cl\cdot C_6H_4Me}$, etc., to tend to increase to the full aliphatic values in the measure in which the M polarisation is cancelled out.

Finally, it may be pointed out that the situation in the halogeno-cymenes is an inversion of that observed in, *e.g.*, 1 : 4-dichloronaphthalene [cf. (I) and (II)], where the $- I$ effects of the chlorine atoms have so depleted the nucleus holding them of electrons that the C–C linkings attaching the second nucleus become permanently polarised—this induced polarisation corresponding to the whole of the measured moment, *i.e.*, to a resultant of *ca.* 0.5×10^{-18} e.s.u. (Weissberger, Sängewald, and Hampson, *Trans. Faraday Soc.*, 1934, **30**, 884) acting in the transverse direction depicted in the formula.

(I.)   (II.)

Relative Activity of p-*Cymene.*—The raising of the electron density and the polarisability of the aromatic nucleus should be reflected in an enhanced activity of those carbon atoms available for substitution, leading to a greater velocity and ease of replacement of nuclear hydrogen by electrophilic reagents in the case of cymene than in that of benzene. Evidence that this is true can be found in the qualitatively observable greater vigour of nitration and ease of halogenation of the former than of the latter. No relevant quantitative data are available, but we have often noticed during iodination and bromination of benzene solutions of cymene, that it is the latter and not the benzene which is principally attacked.

Section III. The Dipole Moment of p-*Ethyltoluene.*—The identical values for the dipole

moments of toluene (Williams, *Physikal. Z.*, 1928, **29**, 174) and of ethylbenzene (Smyth, *J. Amer. Chem. Soc.*, 1924, **46**, 2151) lead one to conclude that the dipole moment of *p*-ethyltoluene should be zero and that the condition of polarisation of this molecule resembles that of *p*-cymene. The following results substantiate this.

p-Ethyltoluene was prepared from redistilled commercial *p*-methylacetophenone by Clemmensen's reduction (Brady and Day, J., 1934, 114); b. p. 162—163°/760 mm., $d_4^{17°}$ 0·8644; $n_D^{25°}$ 1·492505, whence $[R_L]_D = 40·64$. A test with 2 : 4-dinitrophenylhydrazine sulphate in alcohol indicated the absence of unreduced *p*-methylacetophenone.

Molecular Polarisation of Liquid p-*Ethyltoluene.*

Temp. 25°	$d_4^{0°}$	ϵ.	P, c.c.	Temp. 45°	$d_4^{0°}$.	ϵ.	P, c.c.
25°	0·85740	2·23952	40·92	45°	0·83838	2·20225	40·95

Molecular Polarisation of p-*Ethyltoluene in Benzene Solution.*

$10^6 f_1$.	$M_1 f_1 + M_2 f_2$.	ϵ.	$d_4^{25°}$.	$P_1 f_1 + P_2 f_2$.	$P_2 f_2$.	$P_1 f_1$.	P_1.
0	78	2·2725	0·87380	26·5850	26·5850	—	—
40,175·4	79·6873	2·2709	0·87267	27·1726	25·5170	1·6556	41·21
98,639·2	82·1429	2·2666	0·87104	27·9956	23·9627	4·0329	40·89
130,007·1	83·4603	2·2634	0·87016	28·4227	23·1288	5·2939	40·72
150,478·5	84·3201	2·2575	0·86958	28·6401	22·5271	6·1130	40·62

Whence extrapolated P_1 for $f_1 = 0$ is 41·4 c.c.

From the data given by Auwers and Müller (*Ber.*, 1911, **44**, 1607) the molecular refraction for light of infinite wave-length is deduced to be 39·12 c.c.; if the same allowance (2 c.c.) for atomic polarisation be made as in Section I, then $P_E + P_A = 41·12$ c.c., and $P_0 = 41·4—41·12 = 0·28$ c.c. The moment therefore becomes $0·22 \times (0·28)^{1/2} = 0·12 \times 10^{-18}$ e.s.u., which is zero within the limits of experimental error.

However, for the purposes of the substitution experiments previously cited, the methyl and the ethyl group were not thought to have sufficiently contrasted space requirements to produce a marked steric orientation capable of operating against the various polar factors. From other data, the forecast can be made that this hydrocarbon will give on mononitration the 2- and the 3-nitro-derivative in the proportions 57 : 43 (cf. J., 1933, 980), *i.e.*, a much closer approximation to the ideal 50 : 50 ratio than is observed with cymene.

Section IV. The Dipole Moments of tert.-*Butylbenzene and its* p-*Nitro-,* p-*Methyl-, and* 3 : 5-*Dimethyl-derivatives.*—As stated on p. 480, reasons also exist to suggest that *p-tert.*-butyltoluene would not obey all the three conditions there mentioned. For instance, the recorded value of the dipole moment of *tert.*-butyl chloride shows a marked exaltation over that for methyl, ethyl, or propyl chloride (Parts, *Z. physikal. Chem.*, 1930, B, **7**, 327), indicating that the C–Cl bond in the first compound is considerably more polarised than is the corresponding covalency in the last three compounds, presumably because the *tert.*-butyl has a greater polarisability than the other three groups.

Therefore in *p-tert.*-butyltoluene it seemed possible that, in a substitution process of the type defined in Section I, the 3-position could be more activated by an inductive and/or a tautomeric mechanism originating at the butyl group than the 2-position could be by analogous displacements initiated at the methyl radical; *i.e.*, conditions (*b*) and (*c*) might not hold, and the steric might not entirely outweigh the polarisation effects. Relevant cases where this evidently happens are, *e.g.*, the ready formation of a Grignard complex from *o*-bromo- and -iodo-*tert.*-butylbenzenes (Shoesmith and Mackie, J., 1928, 2334), and the preparations of the common artificial musks (trinitro-*tert.*-butyl-toluene or -xylene, etc.), during which nitration ortho to the *tert.*-butyl group is effected without great difficulty; but it is impossible to conclude from Battegay and Haeffely's account of the mononitration of *p-tert.*-butyltoluene (*Bull. Soc. chim.*, 1924, **35**, 981) whether or not this substitution is as unidirectional as the analogous reaction with *p*-cymene (Le Fèvre, *loc. cit.*). At the outset we had hoped to obtain information on the foregoing

points from dielectric polarisation measurements of the types utilised in Sections I and II for the related case of p-cymene, but, owing to the fact that the necessary 2- and 3-monosubstituted derivatives of (V) are unknown (cf. Brady and Lahiri, J., 1934, 1954), this proved impossible; we have therefore undertaken a comparison of the moments of the four *tert.*-butyl compounds (III)—(VI) instead.

CMe$_3$ (III.) NO$_2$—CMe$_3$ (IV.) Me—CMe$_3$ (V.) Me—CMe$_3$—Me (VI.)
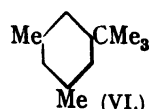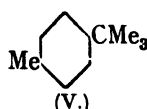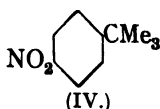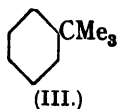
Materials.—tert.-*Butylbenzene* (III). This was prepared from *tert.*-butyl chloride, benzene, and aluminium chloride (Schramm, *Monatsh.*, 1888, **9**, 615); b. p. 167—169°/760 mm., $n_D^{20°}$ 1·50168, $d_4^{20°}$ 0·86733, whence $[R_L]_D$ is 45·57. Richards and Shipley (*J. Amer. Chem. Soc.*, 1919, **41**, 2008) found 2·4 for the dielectric constant of this substance in bulk at 20° and with $\lambda = \infty$; this, combined with $d_4^{20°}$ 0·8671, corresponds to $P = 49·2$ c.c.

p-*Nitro*-tert.-*butylbenzene* (IV). From (III) by direct nitration (Seńkowski, *Ber.*, 1890, **23**, 2416; cf. also Malherbe, *Ber.*, 1919, **52**, 319); b. p. 140—142°/15 mm.

p-tert.-*Butyltoluene* (V). We are indebted to Dr. O. L. Brady and Mr. J. K. Lahiri for a specimen (prepared by Verley's method; *Bull. Soc. chim.*, 1898, **19**, 68); b. p. 76°/15 mm., $d_4^{19°}$ 0·86272, $n_D^{25°}$ 1·489008, $d_4^{25°}$ 0·85968, whence $[R_L]_D$ is 50·3.

5-tert.-*Butyl*-m-*xylene* (VI). From *m*-xylene, *tert.*-butyl chloride, and aluminium chloride (Baur, *Ber.*, 1891, **24**, 2840); b. p. 203—206°/756 mm.

Measurements.—The following tables, except the third, relate to solutions in benzene at 25°.

Molecular Polarisation of tert.-*Butylbenzene.*

$10^6 f_1$.	$M_1 f_1 + M_2 f_2$.	ϵ.	$d_4^{25°}$.	$P_1 f_1 + P_2 f_2$.	$P_2 f_2$.	$P_1 f_1$.	P_1.
0	78	2·2725	0·87380	26·5850	26·5850	—	—
14,323·1	78·8021	2·2768	0·87332	26·9382	26·2042	0·7340	51·25
17,882·0	79·0013	2·2778	0·87323	27·0239	26·1096	0·9143	51·13
28,002·1	79·5681	2·2809	0·87296	27·2725	25·8406	1·4319	51·14
36,462·3	80·0419	2·2834	0·87275	27·4790	25·6157	1·8633	51·10

Whence extrapolated value of P_1 for $f_1 = 0$ is 51·39 c.c.

Molecular Polarisation and Refractivity of p-*Nitro*-tert.-*butylbenzene.*

5,426·7	78·5481	2·4363	0·87624	29·0225	26·4407	2·5818	475·76
21,667·5	80·1884	2·9265	0·88378	35·4812	26·0090	9·4722	437·16
30,012·1	81·0313	3·1781	0·88771	38·3963	25·7872	12·6091	420·13
39,794·8	82·0193	3·4801	0·89234	41·5974	25·5271	16·0703	403·83

Whence extrapolated value of P_1 for $f_1 = 0$ is 490 c.c.

$10^6 f_1$.	$M_1 f_1 + M_2 f_2$.	n.	n^2.	$R_1 f_1 + R_2 f_2$.	$R_2 f_2$.	$R_1 f_1$.	R_1.
0	78	1·49733	2·2400	26·1357	26·1357	—	—
21,667·5	80·1884	1·50002	2·25006	26·69	25·57	1·12	51·7
39,794·8	82·0193	1·50243	2·2573	27·15	25·10	2·05	51·5

Molecular Polarisation of p-tert.-*Butyltoluene.*

Temp.	$d_4^{t°}$.	ϵ.	P, c.c.	Temp.	$d_4^{t°}$.	ϵ.	P, c.c.
0°	0·87940	2·3728	52·83	40°	0·84781	2·2931	52·58
10	0·87160	2·3522	52·76	45	0·84392	2·2824	52·52
20	0·86370	2·3240	52·47	60	0·83204	2·2565	52·51

Molecular Polarisation of p-tert.-*Butyltoluene.*

$10^6 f_1$.	$M_1 f_1 + M_2 f_2$.	ϵ.	$d_4^{25°}$.	$P_1 f_1 + P_2 f_2$.	$P_2 f_2$.	$P_1 f_1$.	P_1.
0	78	2·2725	0·87380	26·5850	26·5850	—	—
11,362·8	78·7954	2·2734	0·87346	26·8813	26·2829	0·5984	52·66
30,077·0	80·1054	2·2749	0·87277	27·3724	25·7854	1·5870	52·76
30,407·5	80·1285	2·2749	0·87276	27·3806	25·7766	1·6040	52·75
36,008·1	80·5206	2·2754	0·87255	27·5287	25·6277	1·9010	52·79

Whence extrapolated P_1 for $f_1 = 0$ is 52·8 c.c.

Molecular Polarisation and Refractivity of 5-tert.-*Butyl*-m-*xylene.*

$10^6 f_1$.	$M_1 f_1 \times M_2 f_2$.	ϵ.	$d_4^{25°}$.	$P_1 f_1 \times P_2 f_2$.	$P_2 f_2$.	$P_1 f_1$.	P_1.
6,896·4	78·5793	2·2723	0·87347	26·7909	26·4017	0·3892	56·44
22,496·4	79·8897	2·2719	0·87270	27·2557	25·9869	1·2688	56·40
12,001·4	79·0081	2·2721	0·87321	26·9422	26·2659	0·6763	56·35
17,999·9	79·5120	2·2720	0·87292	27·1216	26·1065	1·0151	56·39

Whence extrapolated P_1 for $f_1 = 0$ is 56·5 c.c.

$10^6 f_1$.	n.	n^2.	$R_1 f_1 + R_2 f_2$.	$R_2 f_2$.	$R_1 f_1$.	R_1.
0	1·49733	2·2400	26·1357	26·1357	—	—
6,896·4	1·49724	2·24173	26·3358	25·9554	0·3804	55·2
22,496·4	1·49705	2·24116	26·7899	25·5477	1·2422	55·2

Summary of Results.

	P.	$[R_L]_D$.	$\mu \times 10^{18}$.
tert.-Butylbenzene	51·4	45·6	0·53
Nitrobenzene	355	32·7	3·95
p-Nitro-tert.-butylbenzene	490	51·7	4·61
Toluene	33·5	31·1	· 0·34
p-tert.-Butyltoluene	52·8	50·3	0·35
5-tert.-Butyl-m-xylene	56·5	55·2	0·25

In the calculation of the above results no attempt has been made to allow accurately for the atomic polarisation, but, as on p. 482, $P_E + P_A$ has been taken as the molecular refraction for D light, and, in order to give these figures a comparative significance, the moments of nitrobenzene and of toluene, computed from some earlier polarisation measurements made in benzene solution at 25° with our apparatus, are included.

Discussion.—These results appear to indicate that inductive effects are, in fact, operative in this group of compounds. For instance, the higher moment of *tert.*-butylbenzene than of toluene parallels the relationship between the corresponding halides, and illustrates how even the weak $(- I)$ polarising influence of the phenyl group is sufficient to demonstrate the greater ease with which polarisation can be induced in *tert.*-butyl than in methyl; when to this action is added the relayed $(- I)$ effect of a nitro-group in the *p*-position, a further slight exaltation of the moment found over that required by vector addition can be discerned, such superimposition leading, of course, to a moment for 4-nitro-*tert.*-butylbenzene greater than any yet advanced for *p*-nitrotoluene (Williams and Schwingel, *J. Amer. Chem. Soc.*, 1928, **50**, 362; Højendahl, *Physikal. Z.*, 1929, **30**, 391).

The moments of the last two hydrocarbons are difficult to understand, for, not only are they not equal (as required by vectorial principles), but they are unexpectedly high. The possibility that the samples used were mixtures of isomerides is rather small in the first case, in view of the high yields of substitution products, etc., obtained by Brady and Lahiri (*loc. cit.*) on identical material; and in the second instance it is absolutely ruled out by a trinitration of part of the sample of butylxylene used, for this afforded a crude product which, as long boiling with piperidine showed (cf. Le Fèvre and Turner, *J.*, 1927, 1113), certainly did not contain *o*- or *p*-dinitro-groups (as it would have done had the initial hydrocarbon been admixed with 4-butyl-*m*-xylene).

A possible explanation lies in the suggestion (Ingold, *J.*, 1933, 1125) that, during attack on a suitably constituted alkyl compound by a nucleophilic reagent, the alkyl group could be caused to exhibit a $- I$ inductomeric effect (or at least, suffer a diminution of its normal $+ I$ character). If in, say, *p*-*tert.*-butyltoluene, the latter group is regarded as standing permanently towards the rest of the molecule in the same relation as the effective part of a nucleophilic reagent would be during a reaction temporarily towards toluene, a possible mechanism can be envisaged by which the normal Me–C moment becomes depressed; the resultant molecular moment therefore becoming this much larger than would otherwise be the case.

108. 4(5)-β-Alkylaminoethylglyoxalines.

By B. Garforth and F. L. Pyman.

THE preparation of a series of β-*N*-alkylated histamines (III) for comparison of their physiological properties has been impracticable hitherto owing to the difficulty of access to 4(5)-β-hydroxyethylglyoxaline (I), from which they could be readily prepared by way of 4(5)-β-chloroethylglyoxaline (II).
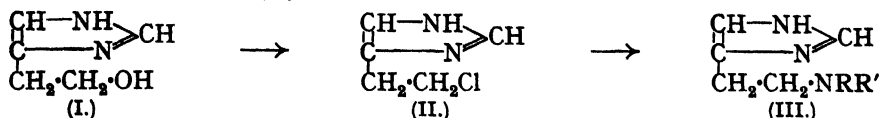
4(5)-β-Hydroxyethylglyoxaline was obtained by the action of barium nitrite upon hist-amine hydrochloride in 19% yield (Windaus and Opitz, *Ber.*, 1911, **44**, 1721), and subse-quently the yield was increased to 64% by Wrede and Holtz (*Pflüger's Archiv*, 1934, **234**, 432), the product being purified as the chloroplatinate in each case. After various alternative syntheses had been attempted without success, an application of Akabori's method (*Ber.*, 1933, **66**, 153; Akabori and Nurmano, *ibid.*, p. 159) of synthesising 4(5)-alkylglyoxalines was tried. *Ethyl α-amino-γ-phenoxybutyrate* was reduced to the crude aminoaldehyde, which, on condensation (as hydrochloride) with ammonium thiocyanate, gave 4(5)-β-*phenoxyethyl-2-thiolglyoxaline* (IV). This readily gave 4(5)-β-*phenoxyethyl-glyoxaline* (V) on oxidation, but dephenoxylation did not proceed satisfactorily and gave only very poor yields of 4(5)-β-hydroxyethylglyoxaline. When, however, α-aminobutyro-lactone hydrobromide (VI) was reduced under the conditions employed by Akabori for the reduction of α-amino-esters, and the product condensed (as salt) with ammonium thiocyanate, 4(5)-β-*hydroxyethyl-2-thiolglyoxaline* (VII) was readily obtained, and gave on oxidation 4(5)-β-*hydroxyethylglyoxaline*, which was now obtained for the first time in crystalline form.
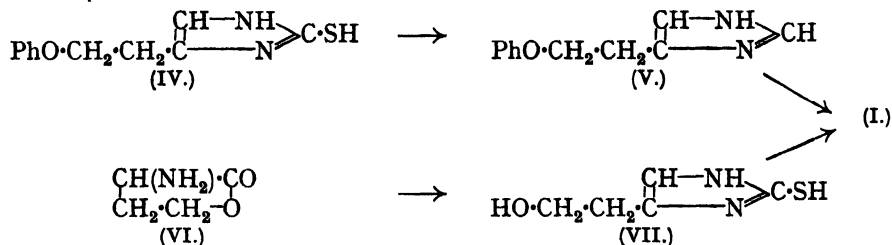
4(5)-β-Hydroxyethylglyoxaline was converted smoothly by means of thionyl chloride into 4(5)-β-*chloroethylglyoxaline hydrochloride* (II), which on heating under pressure with the appropriate amines in alcoholic solution gave histamine, 4(5)-β-*methylaminoethylglyoxaline*, 4(5)-β-*dimethylaminoethylglyoxaline*, 4(5)-β-*trimethylaminoethylglyoxaline chloride hydro-chloride*, and 4(5)-β-*ethylaminoethylglyoxaline*. 4(5)-β-Methylaminoethylglyoxaline was also prepared by the action of 4(5)-chloroethylglyoxaline hydrochloride on *p*-toluene-sulphonmethylamide, followed by hydrolysis of the product. In both cases the dipicrate had m. p. 188° and the dihydrobromide m. p. 167°.

It follows that Fargher and Pyman (*J.*, 1921, **119**, 734) were mistaken in believing that they had obtained 4(5)-β-methylaminoethylglyoxaline by the decarboxylation of *dl*-methylhistidine, for their product formed a dipicrate, m. p. 220°, and a dihydrobromide, m. p. 275°. Moreover, Fargher and Pyman's product had only about one-hundredth of the oxytocic activity of histamine, whereas the true 4(5)-β-methylaminoethylglyoxaline is approximately equal to histamine in its oxytocic action. The physiological actions of the 4(5)-β-alkylaminoethylglyoxalines have been studied by Dr. A. Vartiainen at the National Institute for Medical Research and will be described elsewhere later. Attempts to oxidise 4(5)-β-hydroxyethylglyoxaline to glyoxaline-4(5)-acetaldehyde were unsuccessful (cf. Wrede and Holtz, *loc. cit.*).

K K

EXPERIMENTAL.

α-Amino-γ-phenoxybutyric acid and α-aminobutyrolactone hydrobromide were prepared essentially by the method of Fischer and Blumenthal (*Ber.*, 1907, **40**, 106) from γ-phenoxyethylmalonic acid. This was prepared by the method of Bentley, Haworth, and Perkin (J., 1896, **69**, 161), who give m. p. about 142°, and found to have m. p. 144—145° (corr.; efferv.); Peacock and Tha (J., 1928, 2303), who prepared the acid in a different manner, give m. p. 134—136°.

Bromination of γ-phenoxyethylmalonic acid in dry ether by Fischer and Blumenthal's method is liable to lead to products brominated in the nucleus, and the following method of preparing α-bromo-γ-phenoxyethylmalonic acid was found to be more suitable for work on a larger scale. Phenoxyethylmalonic acid (100 g.) in alcohol-free ether (1200 c.c.) was boiled over a 100-watt lamp in a flask fitted with a good reflux condenser, and bromine (26 c.c.) was slowly added. The bromine was absorbed quickly after approximately 50% had reacted. At the end the ethereal solution was washed with dilute sodium bisulphite solution, then water, the ether removed by distillation, and dry benzene added to the residue and distilled until all the water was removed. On cooling, α-bromo-γ-phenoxyethylmalonic acid crystallised; it was washed with light petroleum. This gave, on decarboxylation, crude α-bromo-γ-phenoxybutyric acid, which gave α-amino-γ-phenoxybutyric acid when heated with aqueous ammonia (*d* 0·91) at 100° in an autoclave. *Ethyl α-amino-γ-phenoxybutyrate hydrochloride*, prepared from the acid, hydrogen chloride and alcohol, crystallised from alcohol in needles, m. p. 210° (corr.) (Found : Cl, 13·7. $C_{12}H_{17}O_3N,HCl$ requires Cl, 13·6%).

4(5)-β-Hydroxyethyl-2-thiolglyoxaline.—α-Aminobutyrolactone hydrobromide (9·0 g.) was dissolved in alcohol (30 c.c.) and water (30 c.c.) and cooled with stirring to below — 15°. Sodium amalgam (3%, 170 g., 4—10 mesh) was added at such a rate as to keep the temperature below — 10°. 5N-Hydrochloric acid was added to keep the mixture faintly acid to Congo-paper throughout the experiment. Stirring was continued for 10 minutes after the last addition of amalgam, then the upper layer was poured off, and the mercury washed with water. To the combined aqueous liquors ammonium thiocyanate (8 g.) was added, followed after 30 minutes by 5N-hydrochloric acid (5 c.c.), and the whole was evaporated to dryness in a vacuum. The residue was extracted three times with alcohol and the united extracts were made acid to Congo-paper with 5N-hydrochloric acid. Water (20—25 c.c.) was added, and the whole concentrated to very low bulk in a vacuum and allowed to cool. On standing or more especially after seeding, *4(5)-β-hydroxyethyl-2-thiolglyoxaline* separated in very variable yield (max., about 55%). Recrystallised from water or alcohol, it formed small colourless plates, m. p. 193° (corr.) (Found : C, 41·9; H, 5·75; N, 19·2; S, 22·5. $C_5H_8ON_2S$ requires C, 41·7; H, 5·6; N, 19·4; S, 22·2%).

It is readily soluble in alcohol or hot water, but very sparingly soluble in ether.

4(5)-β-Hydroxyethylglyoxaline.—4(5)-β-Hydroxyethyl-2-thiolglyoxaline (5 g.) was slowly added to boiling 10% nitric acid (130 c.c.), the reaction, once started, proceeding smoothly with the evolution of brown fumes. The resulting solution was poured on ice, and an excess of phosphotungstic acid (10% w/v in 5% sulphuric acid) added. The whitish precipitate was filtered off and washed, then stirred into boiling water (500 c.c.). Barium hydroxide was added to the solution until it reacted red to brilliant-yellow; the mixture was then filtered hot, treated with carbon dioxide, and a little charcoal added. When the mixture was acid to brilliant-yellow it was filtered hot; the filtrate was evaporated to dryness in vacuum. The colourless gum remaining was dissolved in methyl alcohol, filtered, and again taken to dryness. The first batch solidified only after several months in a desiccator; subsequent batches crystallised readily on seeding (yield, 3·1 g.; 80%). 4(5)-β-Hydroxyethylglyoxaline crystallises from dry chloroform in colourless hexagonal plates, m. p. 92° (corr.) (Found : C, 53·5; H, 7·2; N, 24·95. Calc. for $C_5H_8ON_2$: C, 53·6; H, 7·1; N, 25·0%). It is very readily soluble in water, alcohol or acetone, very sparingly soluble in ether, but insoluble in benzene. The *picrate* separates from concentrated aqueous solution in yellow needles, m. p. 144° (corr.) (Found : N, 20·7. $C_5H_8ON_2,C_6H_3O_7N_3$ requires N, 20·5%). It is soluble in cold water to the extent of about 1·5%. The chloroplatinate and the picrolonate had the m. p.'s recorded by Windaus and Opitz (*loc. cit.*).

4(5)-β-Phenoxyethyl-2-thiolglyoxaline.—α-Amino-γ-phenoxybutyric acid (5 g.) was refluxed for 1 hour with alcohol (75 g.) and hydrogen chloride (5 g.), the alcohol was distilled off, with the addition of dry benzene (50 c.c.), to low bulk, the residue was cooled to — 10° with stirring, and 3% sodium amalgam (80 g.) was gradually added, the solution being kept acid to Congo-paper with dilute hydrochloric acid. At the end the aqueous layer was decanted, the mercury

washed with water, and to the united aqueous liquor ammonium thiocyanate (4 g.) was added. After 1 hour the mixture was evaporated to low bulk; an oil then separated, which was removed and on keeping partly solidified. The addition of a little acetone gave almost pure 4(5)-β-*phenoxyethyl-2-thiolglyoxaline* (2·5 g., 45%). Recrystallised from alcohol, it formed almost colourless needles, m. p. 172° (corr.) (Found : C, 59·9; H, 5·1; N, 12·5; S, 14·2. $C_{11}H_{12}ON_2S$ requires C, 60·0; H, 5·4; N, 12·7; S, 14·5%). Equally good results were obtained by using preformed ethyl α-amino-γ-phenoxybutyrate hydrochloride.

4(5)-β-*Phenoxyethylglyoxaline.*—4(5)-β-Phenoxyethyl-2-thiolglyoxaline (2·5 g.) was slowly added to boiling 10% nitric acid (50 c.c.). When the evolution of brown fumes ceased, the mixture was cooled (an oily nitrate then separated), made alkaline with sodium hydroxide, and extracted with ether. The base was converted into the *hydrochloride* (yield, 1·9 g.; 75%), which crystallised from alcohol–acetone in colourless prismatic needles, m. p. 136—137° (corr.) (Found : N, 12·5; Cl, 15·6. $C_{11}H_{12}ON_2$,HCl requires N, 12·5; Cl, 15·8%). It is very readily soluble in water and alcohol. The oxalate had m. p. 191° (corr.), and the picrate m. p. 122° (corr.). The base regenerated from a pure salt was obtained as a colourless gum which slowly crystallised and then melted at about 70°.

Dephenoxylation.—4(5)-β-Phenoxyethylglyoxaline hydrochloride (1·25 g.) and 85% hydrobromic acid (6 c.c.) were boiled under reflux for 4 hours. The mixture was diluted and distilled in a vacuum to remove phenol. The residue was made alkaline and extracted with ether to remove unchanged phenoxyethylglyoxaline, and the liquor acidified with sulphuric acid and precipitated with phosphotungstic acid. The base, regenerated in the usual way, was converted into the chloroplatinate, which had m. p. 173°, alone or mixed with authentic 4(5)-β-hydroxyethylglyoxaline chloroplatinate. The yield was very small.

4(5)-β-*Chloroethylglyoxaline Hydrochloride.*—4(5)-β-Hydroxyethylglyoxaline (1·2 g.) was treated with thionyl chloride (10 c.c.). The reaction was completed on the steam-bath; the residue after removal of the excess of thionyl chloride rapidly crystallised, in almost theoretical yield. Recrystallised from anhydrous alcohol and ether, 4(5)-*chloroethylglyoxaline hydrochloride* formed colourless hygroscopic needles, m. p. 126° (corr.) (Found : N, 16·5; Cl', 21·5. $C_5H_7N_2Cl$,HCl requires N, 16·7; Cl', 21·3%).

β-*Amino-* and β-*Alkylamino-derivatives of* 4(5)-*Ethylglyoxaline.*—4(5)-β-Hydroxyethylglyoxaline (2·24 g.) was freshly converted into 4(5)-β-chloroethylglyoxaline hydrochloride, which was heated for about 12 hours with 10—15 c.c. of a 30% solution of the appropriate amine in absolute alcohol in a sealed tube at 100°. The product was washed out, treated with a slight excess of sodium carbonate, and taken to dryness in a vacuum. The residue was dissolved in a slight excess of dilute hydrochloric acid and poured into a boiling saturated solution of picric acid (approximately theoretical amount). The dipicrate separated on cooling and was recrystallised from water (charcoal), in which it was sparingly soluble. The picrates, when treated with hydrochloric acid and ether, gave solutions of the dihydrochlorides, which were taken to dryness; the residues were crystallised from absolute alcohol or alcohol–acetone.

4(5)-β-*Methylaminoethylglyoxaline dipicrate* (yield, 60%) crystallises from water in pale yellow, flat needles which lose water at 100° to give opaque orange needles, m.p. 188° (corr.) (Found : loss at 100°, 3·0. $C_6H_{11}N_3,2C_6H_3O_7N_3,H_2O$ requires loss, 3·0%). Found in dried salt : C, 36·8; H, 3·2; N, 21·8. $C_6H_{11}N_3,2C_6H_3O_7N_3$ requires C, 37·0; H, 2·9; N, 21·6%). The *dihydrochloride* is very soluble in water and crystallises from absolute alcohol in colourless needles, m. p. 176—177° (corr.) (Found : C, 36·7; H, 6·4; N, 20·9; Cl, 35·65. $C_6H_{11}N_3,2HCl$ requires C, 36·4; H, 6·6; N, 21·2; Cl, 35·8%). The *dihydrobromide* crystallises from alcohol in colourless needles, m. p. 167° (corr.) (Found : N, 14·7; Br, 55·7. $C_6H_{11}N_3,2HBr$ requires N, 14·7; Br, 55·8%).

4(5)-β-*Dimethylaminoethylglyoxaline dipicrate* (yield, 65%) forms anhydrous orange-yellow plates from water, m p. 233° (corr.) (Found : N, 21·0. $C_7H_{13}N_3,2C_6H_3O_7N_3$ requires N, 21·1%). The *dihydrochloride* crystallises in deliquescent needles from absolute alcohol, m. p. 188° (corr.) [Found : (micro.) C, 39·6; H, 7·05; N, 19·7. $C_7H_{13}N_3,2HCl$ requires C, 39·6; H, 7·1; N, 19·8%].

4(5)-β-*Trimethylaminoethylglyoxaline dipicrate* (yield, 70%) crystallises from water in small orange-yellow needles, m. p. 212° (corr.) [Found : C, 39·5; H, 2·8; N, 20·4. $C_8H_{16}N_3(C_6H_3O_7N_3),C_6H_3O_7N_3$ requires C, 39·3; H, 3·4; N, 20·6%].

4(5)-β-*Trimethylaminoethylglyoxaline chloride hydrochloride* forms extremely deliquescent, colourless needles from absolute alcohol, m. p. 229° (corr.) [Found (micro.) : C, 42·2; H, 7·6; N, 18·3. $C_8H_{16}N_3Cl$,HCl requires C, 42·5; H, 7·5; N, 18·6%].

4(5)-β-*Ethylaminoethylglyoxaline dipicrate* (yield, 55%) crystallises from water in yellow

needles which lose water at 100° to give opaque orange needles, m. p. 186° (corr.) (Found : loss, 5·6. $C_7H_{12}N_2,2C_6H_2O_7N_3,2H_2O$ requires loss, 5·7%. Found in dried salt : N, 21·2. $C_7H_{12}N_2,2C_6H_3O_7N_3$ requires N, 21·1%). The *dihydrochloride* crystallises in colourless plates, m. p. 169° (corr.), from methyl alcohol–acetone [Found (micro.) : C, 39·7, 39·5; H, 7·0, 7·1; N, 19·7; Cl, 33·0. $C_7H_{12}N_2,2HCl$ requires C, 39·6; H, 7·1; N, 19·8; Cl, 33·5%].

4(5)-β-Aminoethylglyoxaline (histamine) was formed when alcoholic ammonia was used in the reaction. It was isolated and identified as the dipicrate, which melted at 238° (corr.), alone or mixed with a reference specimen.

4(5)-β-Methylaminoethylglyoxaline was also prepared by the following method. 4(5)-β-Chloroethylglyoxaline hydrochloride (1·7 g.) was refluxed for 18 hours with alcohol (35 g.), potassium hydroxide (3 g.), and *p*-toluenesulphonmethylamide (5·5g.). The alcohol was removed by distillation, and the residue made alkaline with sodium hydroxide and extracted with ether. The ether on evaporation left a gummy mass, which was dissolved in alcohol (charcoal) and filtered, and the alcohol removed by evaporation. The residue was hydrolysed by heating with sulphuric acid (14 pts.) and water (6 pts.) at 175° for 15 minutes. After cooling and dilution with water, the solution was decolorised with charcoal, rendered alkaline with sodium hydroxide, re-acidified with hydrochloric acid, and taken to dryness in a vacuum. An alcoholic extract of the residue gave with aqueous picric acid 4(5)-β-methylaminoethylglyoxaline dipicrate, which melted at 188° (corr.) alone or mixed with a specimen prepared from 4(5)-β-chloroethylglyoxaline hydrochloride and alcoholic methylamine. Identification was confirmed by the m. p. alone or mixed of the dihydrobromide, 167° (corr.).

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109. *The Preparation of Organic Compounds containing Deuterium. Dideuteromalonic Deuteracid and Trideuteracetic Deuteracid.*

By Christopher L. Wilson.

The preparation of organic compounds containing deuterium in place of protium is most practicable when hydrogen-free substances are allowed to react with reagents containing only deuterium. In this manner the reaction of certain carbides with ' heavy ' water has already been used in the preparation of tetradeuteromethane and dideuteracetylene (Urey and Price, *J. Chem. Physics*, 1934, 2, 300 ; Murray, Squire, and Andrews, *ibid.*, p. 714).

Two reactions involving oxides of carbon offer much better possibilities from a preparative point of view, *viz.*, (1) $CO + NaOD \longrightarrow D \cdot CO_2Na$; (2) $C_3O_2 + 2D_2O \longrightarrow CD_2(CO_2D)_2$. The second of these has been studied because a simple subsequent stage (elimination of carbon dioxide) leads to the formation of the corresponding acetic acid (*trideuteracetic deuteracid*), which can be readily converted into the acid chloride.

Carbon suboxide in benzene solution reacted slowly but completely with an equivalent amount of water having a deuterium content of more than 99·5%. The resulting *dideuteromalonic deuteracid* had an m. p. (128—130°, decomp.) definitely lower than that of ordinary malonic acid (134—135°, decomp.).

Ultimate analysis for carbon and hydrogen established clearly the effect of increased molecular weight. The following table shows the results of such analyses, together with the molecular weight, determined by titration with standard alkali.

Malonic acid.	C, %.	H, %.	D, %.	M.	
From 20% ' heavy ' water	34·3	3·8	—	—	
„ 99·5% „	33·4	—	7·1 *	—	Found
„ „ „	33·3	—	7·1 *	—	
„ „ „ (resublimed)	33·5	—	7·0 *	107·9	
$CH_2(CO_2H)_2$	34·6	3·9	—	104·0	
$CD_2(CO_2D)_2$	33·3	—	7·4	108·1	Calc.
$CH_2(CO_2H)_2 : CD_2(CO_2D)_2 = 4 : 1$	34·3	—	—	—	

* These figures were calculated on the assumption that the water weighed in the combustion was pure D_2O, which, in view of the methods of microanalysis, is probably not true.

The conversion of the malonic acid into the acetic acid by simple heating to 150° was quantitative, making the production of trideuteracetic deuteracid from deuterium oxide substantially quantitative. The product was very pure, judged by the properties of 'light' acetic acid made by the same method. The m. p. (15·8°) was lower than that of 'light' acetic acid (16·6°), but the depression was not as pronounced as in the case of acetic deuter-acid ($CH_3 \cdot CO_2D$), for which Lewis and Schutz (*J. Amer. Chem. Soc.*, 1934, **56**, 493) found 13·3°.

A direct comparison of the vapour pressures of 'light' and 'heavy' acetic acid offers another clear example of a deuterium compound having a higher vapour pressure than its protium analogue. The data (pressures in mm. Hg) are recorded below :

		($p_D - p_P$).				($p_D - p_P$).				($p_D - p_P$).	
T.	p_P.*	Obs.	Calc.†	T.	p_P.*	Obs.	Calc.†	T.	p_P.*	Obs.	Calc.†
20·0°	11·7	0·7	0·7	50·0°	56·6	3·0	3·05	80·0°	202·3	10·3	10·4
25·0	15·5	0·9	0·9	55·0	70·9	3·8	3·8	85·0	243·7	12·4	12·4
30·0	20·6	1·2	1·15	60·0	88·9	4·7	4·7	90·0	293·7	14·7	14·8
35·0	26·8	1·5	1·5	65·0	110·0	5·8	5·8	95·0	349·9	17·4	17·5
40·0	34·8	1·9	1·9	70·0	136·0	7·1	7·1	100·0	417·1	20·8	20·8
45·0	44·4	2·4	2·4	75·0	165·9	8·5	8·6				

* p_P and p_D are the vapour pressures of 'light' and 'heavy' acetic acid respectively, p_P being taken from data of Ramsay and Young (*J.*, 1886, **49**, 790); the intermediate values have been interpolated mathematically.

† The figures in this column are calculated from the equation $\log_{10} p_D/p_P = 3·94/T_{abs.} + 0·0106$.

Lewis and Macdonald (*J. Amer. Chem. Soc.*, 1933, **55**, 3057; cf. Taylor and Jungers, *ibid.*, p. 5057) have attributed the difference of volatility of 'light' and 'heavy' forms of associated substances to the existence of co-ordinated hydrogen bonds; and from the lower volatility of the 'heavy' modifications of such compounds as water and ammonia, which yield associated liquids but unassociated vapours, they inferred that the 'deuterium bond' (—D←) must be stronger than the 'protium bond' (—H←). It can be seen theoretically that, if the co-ordinated bond exists, the difference must be in the direction which Lewis and Macdonald deduced from observation; for this bond must give rise to its own increment in the zero-point energy of the molecule, and since the restoring forces on electrically identical isotopes must be the same, the zero-point energy increment for the co-ordinate bond must be smaller for the heavier hydrogen isotope, the dissociation energy of which will be correspondingly larger.

In contrast to such substances as water and ammonia, the 'light' and 'heavy' forms of compounds which do not associate either as liquid or as vapour have almost identical vapour pressures. Lewis and Schutz (*loc. cit.*) recognised a third class of substance in those which yield definitely associated vapours : these present the interesting possibility that the 'heavy' forms could be more volatile than the 'light.' Hydrogen fluoride and acetic acid, which both yield associated vapours, are now known as illustrations of this effect (Lewis and Schutz, *loc. cit.*; Claussen and Hildebrand, *J. Amer. Chem. Soc.*, 1934, **56**, 1820), and it seems particularly noteworthy that trideuteracetic deuteracid is appreciably more volatile than acetic acid, despite the considerable difference of rotational inertia arising from the terminal distribution of the variable masses, protium and deuterium.

EXPERIMENTAL.

Preparation of Carbon Suboxide.—Diacetyltartaric anhydride (50 g.) (Wohl and Österlin, *Ber.*, 1901, **34**, 1144) was converted into carbon suboxide exactly as described by Hurd and Pilgrim (*J. Amer. Chem. Soc.*, 1933, **55**, 757). The oxide was distilled into a graduated tube cooled to − 78°, the yield being just over 6·3 c.c. (0°) ($d_4^{0°}$ 1·114). Dissolved carbon dioxide was removed by warming to 0° for a few moments. The oxide was stable at − 78° over periods of several days, and in benzene solution it could be preserved at the ordinary temperature for several weeks without polymerisation.

Conversion into Malonic Acid.—'Heavy' water (containing 20% or 99·5% deuterium; about 1 g.) was weighed accurately into a Pyrex tube, 1·5 × 25 cm., sealed at one end and frozen at − 78°. Carbon suboxide (equivalent amount measured by volume) was distilled into the

tube from its graduated container, benzene (10 c.c. per g. of water; dried first by phosphoric oxide and then by standing with carbon suboxide for many days with subsequent distillation, only the middle third being collected) was added, the tube sealed, and shaken at the ordinary temperature. After several days, the tube was opened, and the crystals which had separated were washed with dry benzene and dried over phosphoric oxide at 0·01 mm. The rate of reaction was greatest in the experiment with 20% ' heavy ' water, in which case crystals had appeared after 2 hours. The m. p.'s of the malonic acid from 20% and from 99·5% ' heavy ' water were 131—132·5° and 128—130° (both decomp.), respectively, the latter being unchanged by sublimation at 100°/0·01 mm. The molecular weight of the *dideuteromalonic deuteracid* (10·4 mg.) was determined by titration with $N/100$-sodium hydroxide. The results and other analyses are recorded in the table on p. 492.

Three separate portions of 1 g. of ' heavy ' water were so treated, and each gave an almost quantitative yield of the malonic acid. In one case the product was red, owing to polymerisation of a slight excess of carbon suboxide employed. This impure sample, however, on decomposition as below, gave pure acetic acid.

The benzene used as solvent for the carbon suboxide was thoroughly washed with distilled tap water (no exchange occurs by such treatment; Ingold, Raison, and Wilson, *Nature*, 1934, **134**, 734), dried over anhydrous sodium sulphate, distilled, and burnt over red-hot copper oxide in a stream of nitrogen. Isotopic analysis, by density determination, of the water so obtained failed to show evidence of the occurrence of interchange between the deuterium and the hydrogen atoms of the benzene, within the limit afforded by the accuracy of the pyknometrical measurements ($\pm$ 1 in 10^6; cf. Day, Hughes, Ingold, and Wilson, J., 1934, 1593). This implies that, allowance being made for the proportions in which benzene and deuterium oxide were used, any loss by exchange of deuterium from the deuterium oxide could not have exceeded 0·01 atom %.

Conversion of the Malonic Acid into the Acetic Acid.—The malonic acid was thoroughly dried by heating to 100°/0·01 mm. in the first bulb (A) of an apparatus consisting of three small Pyrex bulbs (each 10 c.c.) connected in series and followed by a phosphoric oxide tube. Rubber connexions were avoided. On immersion of A in a bath at 140—150°, decomposition ensued, and the acetic acid was carried over into the second bulb (B, bubbler type) cooled to 0°. After the tube connecting A and B had been sealed, the acetic acid was purified from a small amount of malonic acid by distillation, without ebullition, at 0·02 mm. into the third bulb C, cooled to 0°, B being maintained at 30°.

' Light ' acetic acid made by this method had m. p. 16·65° (lit. 16·6°). Two different samples of *trideuteracetic deuteracid* had m. p. 15·75° and 15·76° (Found : C, 37·4; D, 12·0. $CD_3 \cdot CO_2D$ requires C, 37·5; D, 12·6%. $CH_3 \cdot CO_2H$ requires C, 40·0; H, 6·7%). The m. p.'s had a range of about 0·2°.

Vapour-pressure Measurements.—A simple differential tensimeter, in which two bulbs similar to C were connected to a U-tube containing pure mercury, was used. By means of an arrangement of taps, both bulbs could be exhausted simultaneously. ' Light ' and ' heavy ' acetic acid (each from the corresponding malonic acid), having been distilled each into one of the bulbs, were alternately frozen with evacuation to 0·01 mm. and liquefied, until all appreciable occluded and dissolved gases had been removed. The bulbs were then sealed off.

The difference in the height of the mercury meniscuses was measured by the use of a cathetometer. Direct readings were obtained from the scale of the latter, and the differences were checked by direct visual estimation by focusing the cathetometer cross-wires on a vertical calibrated glass scale attached to the U-tube. The results of the measurements are summarised in the table on p. 493, the values in col. 3 (accurate to $\pm$ 0·1 mm.) having been interpolated graphically from many readings taken at temperatures slightly above and below the figures quoted.

110. The Magnetic Susceptibility of Cadmium Compounds.

By Winifred R. A. Hollens and James F. Spencer.

DURING the course of an investigation into the nature of the so-called sub-compounds of cadmium (J., 1934, 1062), the scarcity of information concerning the magnetic properties of cadmium compounds was noticed.

Some 30 of these compounds, including the " sub-chloride," were therefore prepared, and measurements of their mass susceptibilities made by the modified Gouy method (Sugden, J., 1932, 161; Trew and Watkins, *Trans. Faraday Soc.*, 1933, **29**, 1310). All the compounds measured were diamagnetic; and the atomic susceptibility of cadmium was also diamagnetic, in keeping with the fact that its atom has a closed configuration. The molecular susceptibility was calculated for each compound, and from it the gram-ionic susceptibility, χ_A, of cadmium. In order to calculate the latter, it was necessary to measure the susceptibilities of other substances, since the values of certain anions required are not recorded in the literature. A mean value of $\chi_A = -24·85 \times 10^{-6}$ was obtained from 30 results. It is interesting to note that the " sub-chloride " gives a value of χ_A which is very close to the mean value above, and this is in accordance with the result (*loc. cit.*) that the substance is a solid solution of metal in cadmic chloride.

EXPERIMENTAL.

Preparation of Materials.—The compounds measured were prepared and purified by the usual methods from Kahlbaum's pure cadmium or A. R. cadmium sulphate. They were all shown to be free from iron by the thioglycollic acid reaction, and from nickel by dimethylglyoxime. The 8-hydroxyquinoline derivative was prepared by Berg's method (*Z. anal. Chem.*, 1927, **71**, 369). The borofluoride, which has not hitherto been described, was obtained by the action of the acid on the carbonate; it was very soluble in water, but sparingly soluble in alcohol and ether. It crystallised as heptahydrate in highly deliquescent needles; dehydration over phosphoric oxide was very slow, requiring about a year for completion. The anhydrous acetate was obtained by refluxing a mixture of cadmium nitrate and acetic anhydride (Späth, *Monatsh.*, 1912, **33**, 235). Cadmium was estimated in the majority of compounds examined by conversion into the sulphate and electrolysis of the solution with a rotating platinum cathode, a current of 1·4—1·6 amps. being used. No compound was employed which gave a cadmium content differing by more than 0·2% from the calculated value.

Measurement of Susceptibility.—This was carried out at atmospheric temperature; six closely agreeing measurements were made with fresh packings in each case, and the mean value recorded. The results are included in Table I, in which χ is the mean measured mass susceptibility, χ_M the g.-mol. susceptibility, δ the susceptibility value of the groups attached to the metallic ion, and χ_A is obtained by subtracting δ from χ_M. Where possible, δ was obtained from values quoted in the " International Critical Tables," VI, 349, and Stoner " Magnetism and Atomic Structure," 1926, p. 122.

TABLE I.

(All values are negative throughout.)

Substance.	χ.	χ_M.	δ.	χ_A.	Substance.	χ.	χ_M.	δ.	χ_A.
Cd	0·167	18·77	0·00	18·77	$Cd_3(PO_4)_2$	0·302	159·20	70·80	29·46†
CdO	0·239	30·70	4·61	26·09	CdC_2O_4	0·265	53·13	28·50	24·60
$Cd(OH)_2$	0·277	40·60	15·30	25·30	$CdH_4C_2O_4,2H_2O...$	0·336	80·90	60·60	20·30
$CdCO_3$	0·271	46·72	22·20	24·52	$Cd(C_2H_3O_2)_2$	0·413	119·90	93·10	26·80
CdS	0·343	49·57	15·60	33·97	$CdC_4H_2O_4$	0·307	58·50	33·70	24·80
$CdSO_4$	0·284	59·23	33·60	25·63	$CdC_4H_4O_4,H_2O$	0·331	68·98	46·70	22·28
$CdSO_4,H_2O$	0·341	77·25	46·60	30·65	$Cd(C_7H_5O_2)_2,2H_2O$	0·476	184·90	162·80	22·10
$3CdSO_4,8H_2O$	0·374	95·94	68·60	27·34	$Cd(C_3H_5O_3)_2$	0·363	83·86	60·00	23·66
$CdCl_2$	0·375	68·74	40·00	28·74	$Cd(C_6H_4·NH_2)_2I_2$	0·426	236·00	221·12	14·88
$CdCl_2,H_2O$	0·428	86·10	53·00	33·10	$CdSO_4(N_2H_5)_2SO_4$	0·367	135·90	107·60	28·30
Cd_4Cl_7	0·357	249·30	140·00	27·32*	$Cd(C_9H_6ON)_2,2H_2O$	0·518	226·10	210·61	15·49
$CdBr_2$	0·320	87·10	62·00	25·10	$Cd(BF_4)_2$	0·351	100·40	81·74	18·66
CdI_2	0·320	117·20	90·00	27·20	$Cd(ClO_3)_2,2H_2O...$	0·272	85·76	78·00	7·76
CdF_2	0·270	40·61	12·60	28·01	$Cd(BrO_3)_2,H_2O...$	0·308	119·00	95·22	23·78
$Cd(NO_3)_2$	0·233	55·10	28·40	26·70	$Cd(IO_3)_2$	0·235	108·40	90·00	18·40
$Cd(NO_3)_2,4H_2O ...$	0·371	114·50	80·40	34·10					

* *I.e.*, $\frac{1}{4} \times 109·30.$ † *I.e.*, $\frac{1}{4} \times 88·40,$

The mean value of χ_A from all the above results is $- 24\cdot85 \times 10^{-6}$.

The data given in Table II were obtained with the object of calculating χ_A in those cases where the literature did not supply the appropriate value of δ. In the determination of δ, the values of gram-atomic susceptibility, $K^\bullet = - 11 \times 10^{-6}$, $Na^\bullet = - 9\cdot2 \times 10^{-6}$, $H = - 3\cdot04 \times 10^{-6}$, were obtained from the same source as δ (above).

TABLE II.

Substance.	χ.	χ_M.	Correction.	Group.	δ.
$C_6H_5NH_2\cdot HI$	$-0\cdot514$	$-113\cdot60$	$- 3\cdot04$	$(C_6H_5\cdot NH_2 + I')$	$-110\cdot56$
KBF_4	$-0\cdot412$	$- 51\cdot87$	$-11\cdot00$	BF_4'	$- 40\cdot87$
$Na_2C_3H_2O_4$	$-0\cdot352$	$- 52\cdot10$	$-18\cdot40$	$CH_2(COO)_2'$	$- 33\cdot70$
$N_2H_4\cdot H_2SO_4$	$-0\cdot437$	$- 56\cdot84$	$- 3\cdot04$	$N_2H_5\cdot SO_4'$	$- 53\cdot80$
C_9H_6NOH	$-0\cdot657$	$- 95\cdot35$	$- 3\cdot04$	C_9H_6ON	$- 92\cdot31$
HIO_3	$-0\cdot267$	$- 48\cdot04$	$- 3\cdot04$	IO_3'	$- 45\cdot00$
$KBrO_3$	$-0\cdot312$	$- 52\cdot11$	$-11\cdot00$	BrO_3'	$- 41\cdot11$

SUMMARY.

1. The mass susceptibilities of 30 cadmium compounds are recorded.
2. The atomic susceptibility of cadmium is found to be $- 24\cdot85 \times 10^{-6}$.
3. Cadmium borofluoride is described.
4. Susceptibility values for the groups $(C_6H_5\cdot NH_2 + I')$, BF_4', $CH_2(COO)_2'$ $N_2H_5\cdot SO_4'$, C_9H_6ON, IO_3', BrO_3' are given.

111. *Derivatives of Naphthalomethylimide.*

By E. M. FRANCIS and J. L. SIMONSEN.

IN view of the fact that naphthalimide and naphthalomethylimide yield perylene derivatives which have found application as dyes (Cain and Thorpe, " Synthetic Dyestuffs," p. 247), it appeared probable that derivatives of the latter might be of value as dye intermediates. We have found, however, that the methylimide is remarkably inert and that it cannot, for example, be condensed with acid chlorides or acid anhydrides by the Friedel–Crafts reaction. 4-*Benzoylnaphthalomethylimide* was prepared indirectly by the action of methylamine on 4-benzoylnaphthalic anhydride (Graebe, *Annalen*, 1903, **327**, 98), but attempts to cyclise it to the corresponding benzanthrone failed.

Nitration of the methylimide resulted in the formation of the 3-*nitro-* or the 3 : 6-*dinitro*-derivative, which were also prepared from 3-nitro- and 3 : 6-dinitro-naphthalic anhydride (Graebe, *loc. cit.,* p. 84; Leuck, Perkins, and Whitmore, *J. Amer. Chem. Soc.,* 1929, **51**, 1831; Rule and Brown, J., 1934, 171) respectively. From 3-*aminonaphthalomethylimide,* the 3-*chloro-* and the 3-*hydroxy*-derivative were prepared. The latter was obtained also from naphthalic anhydride *via* the sulphonic acid (Anselm and Zuckmayer, *Ber.,* 1899, **32**, 3288), thus indirectly orienting the sulphonic acid and the related hydroxy-anhydride.

The condensation of 3-aminonaphthalomethylimide with 1-chloro-, 1-chloro-4-benzamido-, and 1-chloro-5-benzamido-anthraquinone gave 3-1'-*anthraquinonylaminonaphthalomethylimide* (I) and the 4'- and the 5'-*benzamido*-derivative respectively, but cyclisation of these to carbazoles could not be effected (contrast dianthraquinonylamine). In nitrobenzene the reaction proceeded abnormally; with 1-chloroanthraquinone a crystalline *substance,* $C_{36}H_{16}O_4N_4$, was obtained together with anthraquinone. We suggest that this substance is the dihydroazine (II; R = H), the chloroanthraquinone acting as a mild oxidising agent.

Substances of similar type were obtained also when 1-chloro-4-benzamido- and 1-

chloro-5-benzamido-anthraquinone were used as the second component. In addition to 4-benzamidoanthraquinone, crystalline *substances*, $C_{47}H_{27}O_7N_5$, were isolated, which
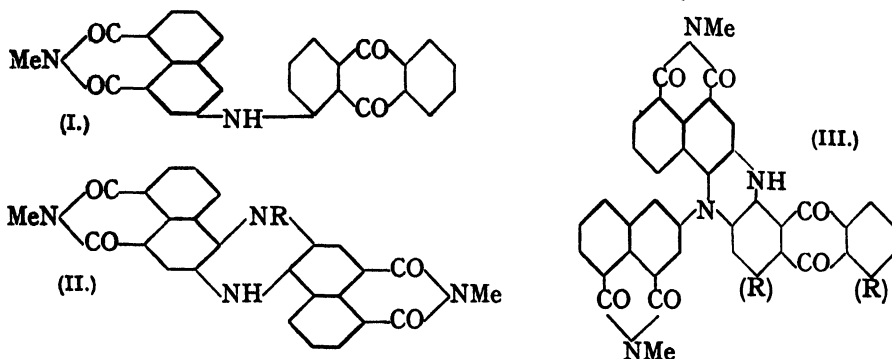
from analogy with (II; R = H) may be represented by either (II; R = 4- or 5-benzamido-anthraquinonyl) or (III; R = H or benzamido-).

3-Chloronaphthalomethylimide did not react with 1-aminoanthraquinone under Ullmann conditions.

Condensation of 3 : 6-*diaminonaphthalomethylimide* with 1-chloro-4-benzamidoanthraquinone in amyl-alcoholic solution resulted in the formation of the *monoanthraquinonyl*-derivative, only one of the amino-groups reacting.

In earlier unpublished experiments by Dr. Fraser Thomson (private communication) it had been observed that the di-imide of perylene-3 : 4 : 9 : 10-tetracarboxylic acid gave on oxidation with manganese dioxide and sulphuric acid a phenol yielding on methylation a substance which was apparently a dimethoxydi-imide. In order to elucidate the structure of this substance, 3-hydroxynaphthalimide (Anselm and Zuckmayer, *loc. cit.*) was fused with potassium hydroxide and the phenol obtained was methylated with methyl sulphate. The dimethyl ether produced must be the perylene derivative (IV; R = R' = OMe, R'' = H or R' = R'' = OMe, R = H). This α-*di-imide* of 1 : 7 (or 1 : 12)-*dimethoxyperylene*-3 : 4 : 9 : 10-*tetracarboxylic acid* differed in colour reactions and dyeing properties from its isomeride, the β-*di-imide*, prepared by the methylation of the phenol produced by direct
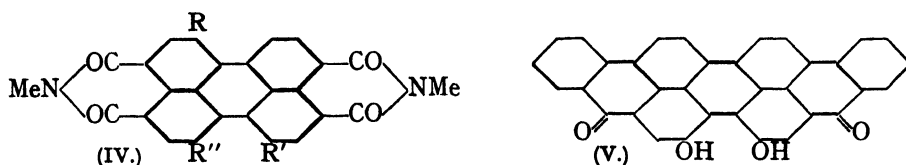
oxidation of the perylene. The positions of the methoxy-groups in the latter compound therefore remain undetermined but it seems not improbable that the two ethers are the isomerides (IV; R = R' = OMe, R'' = H) and (IV; R' = R'' = OMe, R = H), since in the somewhat analogous case of dibenzanthrone treatment with manganese dioxide and sulphuric acid results in the formation of the dihydroxydibenzanthrone (V).

<div align="center">EXPERIMENTAL.</div>

3-Nitronaphthalomethylimide.—To a gently boiling solution of naphthalomethylimide (20 g.) in acetic acid (300 c.c.) a mixture of acetic acid (100 c.c.) and nitric acid (*d* 1·5; 100 c.c.) was added during 20 minutes; after further boiling for 1 hour, water (100 c.c.) was added. When the combined products from five such operations were kept over-night, a crystalline solid (*A*) (50 g.; m. p. 213—217°) separated, repeated crystallisation of which from acetic acid gave 3-*nitronaphthalomethylimide* in fine needles, m. p. 226—228° (Found : C, 61·2; H, 3·4; N, 11·4. $C_{13}H_6O_4N_2$ requires C, 60·9; H, 3·1; N, 10·9%). Dilution with water of the filtrate from *A* deposited a mixture of the nitro-compound and unchanged imide. 3-*Nitronaphthalimide*, prepared by digestion of 3-nitronaphthalic anhydride with aqueous ammonia (*d* 0·88) for 1

hour, crystallised from nitrobenzene in small needles, m. p. 308° (sintering at 305°) (Found : N, 11·9. $C_{12}H_6O_4N_2$ requires N, 11·6%). Methylation of the imide in nitrobenzene solution with methyl sulphate and potassium carbonate gave 3-nitronaphthalomethylimide, m. p. 225—227° alone and in admixture with the above product.

3-*Aminonaphthalomethylimide.*—Sodium hydrosulphite (20 g. and after 1 hour a further 20 g.) was added to a stirred boiling solution of the 3-nitro-methylimide (10 g.) in alcohol (200 c.c.) and water (20 c.c.). Heating was continued an hour longer, the alcohol then evaporated, the residue mixed with an excess of dilute hydrochloric acid, and the filtered solution basified. The *amine* (9 g.) was crystallised from nitrobenzene and three times from xylene, forming fine yellow needles, m. p. 278—280° (Found : C, 68·9; H, 4·8. $C_{13}H_{10}O_2N_2$ requires C, 69·0; H, 4·4%). The diazonium sulphate of the base coupled with β-naphthol to yield the *azo*-derivative, crystallising from nitrobenzene in small red needles, m. p. 315—317° (Found : N, 11·4. $C_{23}H_{15}O_3N_3$ requires N, 11·3%). The *acetyl* derivative of the base separated from nitrobenzene in needles, m. p. 329—330° (Found : N, 11·0. $C_{15}H_{12}O_3N_2$ requires N, 10·4%).

3-*Hydroxynaphthalomethylimide.*—A mixture of sulphuric acid (d 1·84; 10 c.c.) and sodium nitrite (0·95 g.) was added to a cooled solution (salt–ice) of the preceding amine (3 g.) in sulphuric acid (d 1·84; 20 c.c.), and phosphoric acid (d 1·7; 45 c.c.) run into the stirred mixture. After 30 minutes the product was poured on ice and the diazo-solution was added during 1 hour to a vigorously stirred mixture of sulphuric acid (20 c.c.), water (80 c.c.), and tetrachloroethane (100 c.c.) in a bath at 110—120°. Heating was continued for a further 15 minutes, the tetrachloroethane separated from the hot aqueous layer, and the latter again extracted with hot tetrachloroethane. The combined extracts were distilled in steam and the solid (2 g.) remaining was sublimed in a low vacuum. The *hydroxy-methylimide* then crystallised from dichlorobenzene in yellow needles, m. p. 272—273° (Found : N, 6·2. $C_{13}H_9O_3N$ requires N, 6·2%). 3-*Chloronaphthalomethylimide*, purified by repeated crystallisation from alcohol (charcoal), separated in needles, m. p. 182—183° (Found : Cl, 14·2. $C_{13}H_8O_2NCl$ requires Cl, 14·5%).

Condensations of 3-*Aminonaphthalomethylimide.*—(a) *With* 1-*chloroanthraquinone.* (i) In amyl alcohol. A mixture of the base (6 g.), 1-chloroanthraquinone (7 g.), cupric chloride (1·5 g.), sodium acetate (7 g.), and amyl alcohol (50 c.c.) was heated at 160—170° for 16 hours. After removal of the amyl alcohol in steam, the solution was digested with dilute hydrochloric acid to dissolve unchanged base (5 g.), and the brown residue boiled with alcohol (160 c.c.); the undissolved portion (4·7 g.) crystallised from pyridine as a brown powder of microscopic needles of 3-1-*anthraquinonylaminonaphthalomethylimide* (I), m. p. 286—287° (Found : C, 74·0, 74·1; H, 4·1, 4·0; N, 6·6. $C_{27}H_{16}O_4N_2$ requires C, 75·2; H, 3·7; N, 6·5%).* This substance dyes cotton, for which it has little affinity, a weak brown colour from a pink vat.

(ii) In nitrobenzene. Similar quantities of the reactants were heated in nitrobenzene at 200—210° for 7 hours. After steam-distillation and extraction with dilute hydrochloric acid, the residue (8 g.) was crystallised twice from aniline, giving a mixture, m. p. 275—280°, of microscopic plates and needles. Recrystallisation from pyridine, which left undissolved a sparingly soluble *substance* (*A*), gave yellow needles, m. p. 275°, of anthraquinone. *A*, after digestion with nitrobenzene, crystallised from *o*-toluidine in purple-red plates, m. p. above 400° (Found : C, 69·5; H, 4·4; N, 12·1. $C_{26}H_{16}O_4N_4$ requires C, 69·6; H, 3·6; N, 12·3%). The possible structure of this substance is discussed on p. 496.

(b) *With* 1-*chloro-5-benzamidoanthraquinone.* (i) In amyl alcohol. A mixture of the amine (5 g.), 1-chloro-5-benzamidoanthraquinone (9 g.), sodium acetate (7 g.), cupric chloride (2 g.), and amyl alcohol (200 c.c.) was heated for 7 hours in an autoclave at 3 atms. After removal of the alcohol in steam and extraction with 10% hydrochloric acid to remove unchanged base (4 g.) and with acetic acid, the residue (0·6 g.) was repeatedly crystallised from pyridine, the 5'-*benzamido*-derivative of (I) separating in red needles, m. p. 338—339° (Found : C, 73·6; H, 4·4; N, 7·8. $C_{34}H_{21}O_5N_3$ requires C, 74·1; H, 3·8; N, 7·6%).

(ii) In nitrobenzene. A similar mixture of the reactants in nitrobenzene (100 c.c.) was heated at 210° for 7 hours. The neutral product, after extraction with chlorobenzene, left a red crystalline residue (X), and the solution deposited a solid, which had m. p. 244—246°, after crystallisation from chlorobenzene and was identified as 1-benzamidoanthraquinone by hydrolysis to 1-aminoanthraquinone, m. p. 243°. The solid (X) (II or III) crystallised from nitrobenzene in microscopic red needles, m. p. 331—333° (Found : C, 73·0; H, 4·0; H, 9·1. $C_{47}H_{27}O_7N_5$ requires C, 73·0; H, 3·5; N, 9·1%).

* The majority of the substances described in this paper were very difficult to burn and good results were not obtained in microanalyses.

(c) *With 1-chloro-4-benzamidoanthraquinone.* (i) In amyl alcohol. Condensation of the base with the chloroanthraquinone was effected by heating at 170—180° for 7 hours, the quantities of reactants being as given above. The 4′-*benzamido*-derivative of (I) crystallised from pyridine in mauve needles, m. p. 330—331° (Found : C, 74·0; H, 4·2; N, 7·9%).

(ii) In nitrobenzene. The *substance* (II or III) was obtained in small yield and crystallised from nitrobenzene in purple needles, m. p. 320—323° (Found : N, 8·9%). Much 1-benzamido-anthraquinone was formed simultaneously.

3 : 6-*Dinitronaphthalomethylimide.*—To a solution of the *N*-methylimide (5 g.) in acetic anhydride (100 c.c.), nitric acid (*d* 1·5; 35 c.c.) was added at a rate sufficient to keep the solution gently boiling. The cooled solution deposited a solid (2·2 g.) m. p. 258—265°, from which after renitration under conditions similar to those described above, 3 : 6-*dinitronaphthalomethyl-imide* was obtained, which crystallised from acetic acid in pale yellow needles, m. p. 280° (Found : C, 52·3; H, 2·4. $C_{13}H_7O_6N_3$ requires C, 51·8; H, 2·3%). This substance was prepared also by the digestion of 3 : 6-dinitronaphthalic anhydride with dilute aqueous methylamine. The *diamine*, obtained by the reduction of the dinitro-methylimide with sodium hydrosulphite, crystallised from aniline in golden-yellow needles, m. p. above 400° (Found : N, 17·7. $C_{13}H_{11}O_2N_3$ requires N, 17·4%). The *diacetyl* derivative separated from acetic acid in yellow needles, decomp. 383—384° (Found : N, 12·9. $C_{17}H_{15}O_4N_3$ requires N, 12·9%). Condensation with 1-chloro-4-aminobenzoylanthraquinone in amyl-alcoholic solution gave the 4-*benzamido-anthraquinonyl*-derivative, crystallising from aniline in blue needles, m. p. 295—297° (sintering at 280°) (Found : N, 9·8. $C_{34}H_{22}O_5N_4$ requires N, 9·9%). It dyed cotton a weak grey shade from a port-wine coloured vat.

4-*Benzoylnaphthalomethylimide*, prepared by the digestion of 4-benzoylnaphthalic anhydride (Graebe, *loc. cit.*, p. 98) with dilute aqueous methylamine, crystallised from toluene in needles, m. p. 190—191°, and dissolved in sodium hydrosulphide to yield a red solution (Found : C, 76·4; H, 4·3. $C_{20}H_{13}O_3N$ requires C, 76·2; H, 4·1%).

α-*Di-imide of* 1 : 7 (or 1 : 12)-*Dimethoxyperylene-*3 : 4 : 9 : 10-*tetracarboxylic Acid* (IV).—A mixture of 3-hydroxynaphthalimide (12 g.), potassium hydroxide (100 g.), and ethyl alcohol (100 c.c.) was gradually heated to 230° in a nickel basin and with occasional stirring kept at this temperature for 2 hours. The cooled melt, after solution in water, was acidified and the purple solid (12 g.) which separated was collected. The phenol, which was insoluble in all the ordinary solvents, could not be purified. Its solution in sodium hydroxide was bright green and in sulphuric acid bluish-green. For the preparation of the dimethyl ether, the phenol (12 g.) with nitrobenzene (100 c.c.) and sodium carbonate (20 g.) was heated at 210°, and methyl sulphate (10 g.) added to the stirred mixture. At intervals of 1 hour three similar quantities of sodium carbonate and methyl sulphate were added and after one further hour the nitrobenzene was removed in steam and the residue digested with sodium hydroxide solution (10%) to dissolve unchanged phenol. The α-*di-imide* (5 g.) after four crystallisations from nitrobenzene separated in long slender black needles, m. p. above 400° [Found : C, 69·9; H, 4·0; OMe, 14·7. $C_{24}H_8O_4N_2(OMe)_2$ requires C, 69·4; H, 3·1; OMe, 14·2%]. The ether dissolved in sulphuric acid to yield a green solution; the alkaline hydrosulphite vat was blue and dyed cotton a bright purple to lilac colour.

β-*Di-imide of* 1 : 7 (or 1 : 12)-*Dimethoxyperylene-*3 : 4 : 9 : 10-*tetracarboxylic Acid*(?).—To a solution of the di-imide of perylene-3 : 4 : 9 : 10-tetracarboxylic acid (10 g.) in sulphuric acid (*d* 1·84; 400 g.) containing boric acid (10 g.), manganese dioxide (82%; 12·7 g.) was added; heat was evolved and the solution became blue. After 1 hour at 60° (stirring) the product was added to ice and sodium bisulphite (20 g.), and the solid collected. The phenol dissolved in sulphuric acid to give a blue solution. After methylation under conditions similar to those described for the α-di-imide, the product was recrystallised from nitrobenzene, the β-*di-imide* being obtained in black needles, m. p. above 400°. It dissolved in sulphuric acid to give a blue solution having a faintly green tinge; it dyed cotton a slightly redder shade than its isomeride (Found : C, 69·2; H, 4·4%).

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112. *The Synthesis of Polyterpenoid Compounds.* Part I. *Preliminary Experiments.*

By J. W. COOK and A. DANSI.

METHODS recently developed in this and other laboratories for the synthesis of hydrogenated phenanthrene derivatives necessarily give products which contain at least one aromatic ring, a circumstance which precludes the general extension of such methods to the synthesis of many of the naturally occurring polycyclic compounds. However, it is well known that terpenoid compounds often readily undergo cyclisation by interaction of pairs of ethylenic bonds within the molecule. The purpose of this series of memoirs is to present methods of synthesis of compounds containing two double bonds suitably disposed for cyclisation to polycyclic hydroaromatic compounds. The outcome of the experiments now described has not been very satisfactory, partly on account of the difficulty of isolating homogeneous substances in the later stages of the syntheses, and partly on account of the unexpected resistance to cyclisation shown by the synthetic dienes. Nevertheless, it is desired to place on record the procedure adopted in the synthesis of such dienes, and it is proposed to extend these methods to compounds in which a methyl group is attached to one of the unsaturated carbon atoms at which cyclisation should occur. Experience with other types of compound (Cook, Hewett, Mayneord, and Roe, J., 1934, 1727) encourages the belief that the presence of such methyl groups will facilitate cyclisation. This is also suggested by the presence of similarly disposed methyl groups in the terpenes which so readily undergo cyclisation, even by boiling with formic acid; for example, α-camphorene (Ruzicka and Stoll, *Helv. Chim. Acta*, 1924, **7**, 271) and squalene (Heilbron, Kamm, and Owens, J., 1926, 1641).

Bouveault reduction of ethyl Δ^1-*cyclo*hexenylacetate led to the anticipated β-Δ^1-*cyclohexenylethyl alcohol* (I; R′ = R″ = H), the βγ-double bond being unattacked by sodium and alcohol. The Grignard compound of the corresponding *bromide* was treated with (a) *cyclo*hexanone and (b) α-tetralone. The resulting crude carbinols were dehydrated to the corresponding dienes, that from α-tetralone, for example, being represented in all probability by structure (II), for it is well known that dehydration of cyclic carbinols leads to an endocyclic rather than an exocyclic double bond.

(I.) $\quad$ CHR′·CH$_2$·OH $\qquad$ (II.)

R″
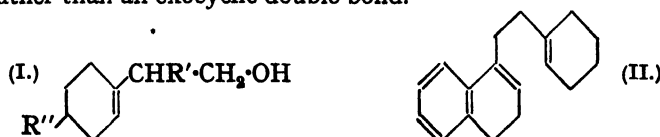
Attempts to cyclise (II) to a decahydrochrysene by prolonged heating with 98% formic acid were unsuccessful, and the bromine absorption value of the analogous diene obtained from *cyclo*hexanone was not appreciably diminished by 24 hours' boiling with formic acid. Partial cyclisation of (II) was effected by boiling acetic acid containing sulphuric acid, the reaction being accompanied by much resinification. The unpolymerised product gave chrysene when dehydrogenated with selenium.

Bouveault reduction of ethyl α-(4-methyl-Δ^1-*cyclo*hexenyl)propionate gave β-(4-methyl-Δ^1-*cyclo*hexenyl)-*n*-propyl alcohol (I; R′ = R″ = Me). No sesquiterpenoid hydrocarbon could be obtained from the products of interaction of *iso*valeraldehyde with the Grignard solution prepared from the bromide of this alcohol.

EXPERIMENTAL.

β-Δ^1-*cycloHexenylethyl Alcohol* (I; R′ = R″ = H).—The Reformatsky reaction with *cyclo*hexanone was carried out in benzene solution (Wallach, *Annalen*, 1905, **343**, 51; 1906, **347**, 328), Kahlbaum's ethyl bromoacetate being used. In spite of many attempts we were unable to effect any condensation with ethyl bromoacetate supplied by British Drug Houses, Ltd. Dehydration of ethyl *cyclo*hexanol-1-acetate to ethyl Δ^1-*cyclo*hexenylacetate was only partially effected with potassium hydrogen sulphate (contrast Auwers and Ellinger, *Annalen*, 1912, **387**,

228). The incompleteness of the dehydration was probably due to some peculiarity of the potassium hydrogen sulphate with which we were unfortunate enough to be supplied, for one of us (J. W. C.) has repeatedly failed to effect complete dehydration with this material (which was well fused immediately before use) of divers carbinols for which the successful use of potassium hydrogen sulphate had been claimed in the literature. Dehydration of ethyl *cyclo*hexanol-1-acetate (36 g.) was successfully accomplished by 2½ hours' heating on the water-bath with phosphoric oxide (50 g.) in benzene (150 g.).

Sodium (66 g.) was gradually added to a boiling solution of ethyl Δ¹-*cyclo*hexenylacetate (80 g.) in ethyl alcohol (380 g.), the temperature of the bath being gradually raised to 130° during addition, and maintained at this point for 7 hours. Water was cautiously added until the excess of sodium was destroyed. A large volume of water was then added, and the cold liquid repeatedly extracted with ether. The extract was dried (sodium sulphate), the ether and most of the ethyl alcohol distilled through a fractionating column, and the residue cautiously distilled in steam until the last traces of ethyl alcohol had been removed. The *cyclo*hexenylethyl alcohol was then again extracted with ether and distilled in a vacuum. It formed a colourless pleasant-smelling liquid, b. p. 85—90°/8 mm. (yield, 55%), and absorbed the amount of bromine required for one double bond (method of Rosenmund and Kuhnhenn, *Z. Unters. Nahr. Genussm.*, 1923, 46, 154).

β-Δ¹-*cyclo*Hexenylethyl 3 : 5-*dinitrobenzoate*, formed by brief warming at 100° with 3 : 5-dinitrobenzoyl chloride in pyridine, formed colourless needles (from alcohol), m. p. 80° (Found : C, 56·1; H, 5·0. $C_{15}H_{16}O_6N_2$ requires C, 56·2; H, 5·0%). β-Δ¹-*cyclo*Hexenylethyl alcohol, obtained by hydrolysis of the pure dinitrobenzoate, gave low values for carbon, probably on account of oxidation at the expense of the potassium dinitrobenzoate (compare Hückel and Kumetat, *Ber.*, 1934, 67, 1890) (Found : C, 75·3; H, 11·7. $C_8H_{14}O$ requires C, 76·2; H, 11·2%).

β-Δ¹-*cyclo*Hexenylethyl Bromide.—Phosphorus tribromide (14 g.) was slowly added to an ice-cold mixture of the alcohol (17 g.), ligroin (20 g.), and pyridine (1 c.c.). After being kept at 0° for 2 hours, the whole was treated with water, and the oily layer separated, washed with water and dilute sodium carbonate solution, dried (calcium chloride), and distilled in a vacuum. The *bromide* (yield, 50%) formed an unstable colourless liquid, b. p. 90°/7 mm. (Found : C, 50·3; H, 7·3. $C_8H_{13}Br$ requires C, 50·8; H, 6·9%).

β-(4-Methyl-Δ¹-*cyclo*hexenyl)-n-propyl alcohol was obtained by reduction with sodium and ethyl alcohol of ethyl α-(4-methyl-Δ¹-*cyclo*hexenyl)propionate (Wallach, *Annalen*, 1908, 360, 52), exactly as in the case of the lower homologue. It formed a colourless, viscous, pleasant-smelling liquid, b. p. 105—109°/10 mm. (yield, 35%), and gave a 3 : 5-*dinitrobenzoate*, which crystallised from alcohol in colourless needles, m. p. 71° (Found : C, 58·4; H, 5·9. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·8%). The free alcohol absorbed the amount of bromine required for one double bond. The *bromide*, prepared by the method described above, was a very unstable, colourless liquid, b. p. 95—100°/10 mm., having a camphor-like smell (Found : C, 57·1; H, 8·3. $C_{10}H_{17}Br$ requires C, 55·3; H, 7·9%).

Attempted Synthesis of Dodecahydrophenanthrene.—A mixture of β-Δ¹-*cyclo*hexenylethyl bromide (16 g.) and anhydrous ether (50 c.c.) was added during an hour to a large excess of magnesium (5 g.), the liquid being kept vigorously boiling. Under other conditions very poor yields of Grignard compound were obtained. The clear solution was decanted from the excess of magnesium, cooled in ice, and treated dropwise with *cyclo*hexanone (8·5 g.). After being kept at room temperature over-night, the product was decomposed (ice and ammonium chloride), washed, dried (sodium sulphate), and distilled at 5 mm. β-Δ¹-*cyclo*Hexenylethylcyclohexanol, which could not be obtained analytically pure, formed a colourless, somewhat viscous liquid, b. p. 89—91°/0·3 mm., with a faint orange-like smell (Found : C, 82·8; H, 11·5. $C_{14}H_{24}O$ requires C, 80·7; H, 11·6%). Dehydration with potassium hydrogen sulphate was incomplete; the resulting colourless liquid, after distillation over sodium, had b. p. 97—98°/4—5 mm. (Found : C, 86·7; H, 12·1. $C_{14}H_{22}$ requires C, 88·3; H, 11·7%). No change in the bromine absorption value was brought about by 24 hours' boiling with 98% formic acid (4 parts), and subsequent heating with selenium at 300—310° for 16 hours did not result in dehydrogenation (Found, after redistillation over sodium : C, 88·5; H, 11·2%). The significance of the latter observation need not be discussed at present, as an investigation of other hydroaromatic compounds resistant to the dehydrogenating action of selenium is in progress.

Formation of Chrysene.—A Grignard solution prepared from β-Δ¹-*cyclo*hexenylethyl bromide (9·4 g.) was treated with α-tetralone (7·25 g.) and then boiled for 2 hours. After decomposition with ice and ammonium chloride the ethereal solution was washed, dried, and distilled. The

crude carbinol fraction (3·5 g.; b. p. 140—175°/6 mm.) was heated at 160—170° for 2 hours with potassium hydrogen sulphate, and the product redistilled in a vacuum. The bromine absorption value was in agreement with formula (II). Attempted cyclisation with formic acid under various conditions (*e.g.*, by heating on the water-bath for 24 hours with 98% acid) led to no change in the bromine absorption value, and subsequent dehydrogenation with selenium gave no more than a trace of chrysene. When the hydrocarbon (II) (1 g.) was boiled for 5 hours with concentrated sulphuric acid (1 c.c.) in acetic acid (10 c.c.), much resinification took place. After extraction with ether and distillation in a vacuum, 0·2 g. of an oil was obtained, and this gave 20 mg. of pure chrysene (identified by comparison with an authentic sample) after dehydrogenation with selenium.

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113. *The Dipole Moments of Associated Liquids.*

By FRANK R. GOSS.

THE influence of a liquid medium in reducing the observed polarisation of a polar substance in solution was formerly ascribed (Debye, Marx's "Handbuch der Radiologie," Leipzig, 1925, VI, 633) to association of the polar molecules; Bury and Jenkins (J., 1934, 688), however, pointed out that, to accord with Sidgwick's views ("Electronic Theory of Valency," Oxford, 1927, 132), association should lead to an increase instead of a decrease in polarisation, as indeed has been experimentally observed in the case of the alcohols (cf. Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312); it has further been shown (Goss, J., 1934, 696) that decrease in polarisation, where it is observed, can be explained by the effect of the anisotropy of the polarisation field. It seems possible, therefore, that the variations in the polarisation of solutes with concentration may be due to the opposing effects of anisotropy and association, causing respectively decreases and increases in the polarisation of substances in the liquid state.

We consider anisotropy first. The Clausius–Mosotti expression

$$(\varepsilon - 1)/(\varepsilon + 2) = 4\pi\nu\alpha/3 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

which connects the dielectric constant ε with α, the polarisability of the molecules, and ν, the number of molecules per unit volume, is theoretically valid only for a symmetrical polarisation field. It has been experimentally verified for gases (Uhlig, Kirkwood, and Keyes, *J. Chem. Physics*, 1933, **1**, 155; Michels and Michels, *Phil. Trans.*, 1934, *A*, **231**, 409) and expressed in a form applicable to an anisotropic polarisation field (Raman and Krishnan, *Proc. Roy. Soc.*, 1928, *A*, **117**, 595), *viz.*,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\nu \frac{\frac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3)}{1 - \frac{1}{3}\nu(\alpha_1 s_1 + \alpha_2 s_2 + \alpha_3 s_3)} \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

where α_1, α_2, α_3 are components of α, and s_1, s_2, s_3 are the component amounts by which the polarisation field varies from the values it would have if it were isotropic.

The Raman–Krishnan formulæ express in theoretical terms the experimental facts that (*a*) the electron and atom polarisations of all liquids increase slightly with temperature (cf. Goss, J., 1933, 1341), (*b*) the calculated polarisation *P* of a polar solute varies with its concentration in solution (cf. van Arkel and Snoek, *Rec. trav. chim.*, 1932, **51**, 1081), and (*c*) the polarisation of such a solute at infinite dilution *P* varies as the solvent is changed (cf. Muller, *Physikal. Z.*, 1933, **34**, 689), with the consequence that dipole moments calculated directly from solution data by Debye's formula ("Polare Molekeln," Leipzig, 1929, 56), which is based on the expression (1), may vary with the solvent, and usually differ from the moments calculated from measurements on the gaseous state (cf. Smyth, *J. Chem. Physics*, 1932, **1**, 247).

The theoretical expression for the components of the observed polarisation P_2 of a non-associating substance, either as a pure liquid or as a component of a non-associating liquid mixture, may conveniently be written (cf. Goss, *loc. cit.*)

$$P_2 = P_{E+A+O} - pA_{E+O} \quad \cdots \cdots \cdots (3)$$

where P_{E+A+O} represents the molar polarisations which the substance would have in the gaseous state, p is the polarisation of the medium per unit volume $[p = (\epsilon - 1)/(\epsilon + 2)]$, and A_{E+O} is the molar anisotropy factor. A_{E+O} represents the sum of two factors $A_E = - N\psi$ and $A_O = - N^2\Theta/3RT$, which are respectively the amounts by which the distortion and the orientation polarisation, P_{E+A} and P_O, are reduced by the anisotropy of the local field, ψ and Θ have the significance given in the Raman–Krishnan theory (*q.v.*), N is the Avogadro number, R is the gas constant, and T the absolute temperature. This expression can be applied to methyl chloride (see Fig. 1), but is evidently only valid for the simplest non-associating molecules.

FIG. 1.
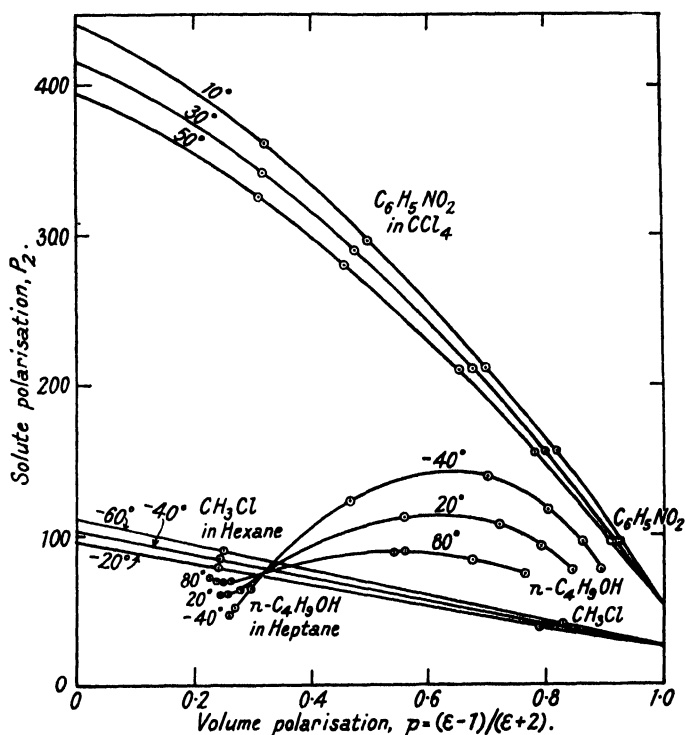
In order to explain the polarisation of more complex substances, Sugden (*Nature*, 1934, **133**, 415) introduced an addition P_a to those terms which are independent of temperature, so that the polarisation of liquids could be expressed as

$$P_2 = P_{E+A+O} + P_a - pA_{E+O} \quad \cdots \cdots \cdots (4)$$

This formula, however, is found to be inapplicable to the published data for many substances, including ether and chloroform (Goss, *loc. cit.*), nitrobenzene (this paper), and alcohol (Smyth and Stoops, *loc. cit.*).

Subbaramaiya (*Proc. Indian Acad. Sci.*, 1934, *A*, **1**, 355) has discussed the effect of the anisotropy terms on the usual mixture rule for the polarisation of liquids, *viz.*,

$$P_{12} = P_1c_1 + P_2c_2 \quad \cdots \cdots \cdots (5)$$

where P_{12} is the polarisation of the mixture, P_1 that of the solvent, and c_1, c_2 the molar con-

centrations of the solvent and the solute respectively. It seems desirable, therefore, to consider the effect of introducing terms arising from association. If the additional polarisations arising from the association of the solvent and of the solute are represented by K_1 and K_2 respectively, and that which the solute would have if it were not associated is denoted by P'_2, then, provided K_1 be small compared with P_1,

$$P_{12} = P_1 c_1 + P'_2 c_2 + K_1 c_1 + K_2 c_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Combining this with expression (5), we have

$$P_2 = P'_2 + K_2 - K_1 c_1/c_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Now it is evident that, for an associated liquid, expression (4) must be written as

$$P'_2 = P_{E+A+O} + P_a - pA_{E+O} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

whence $$P_2 = P_{E+A+O} + P_a - pA_{E+O} + K_2 - K_1 c_1/c_2 \quad . \quad . \quad . \quad (9)$$

If now K_1 has a value other than zero, and the expression (9) is extrapolated to values of p for which either c_1 or c_2 is less than zero, the values obtained for the polarisation terms will have no real significance. Fairbrother (J., 1934, 1846) has shown that extrapolation of the observed relationship between P_2 and p for nitrobenzene in p-xylene solution does, in fact, lead to unexpectedly high values of P_{E+A+O}.

Values for the polarisation of nitrobenzene in carbon tetrachloride, which may be regarded as essentially a non-associating solvent, have been provided by Pal (*Phil. Mag.*, 1930, **10**, 265), and these can be represented very closely by $P_2 = a - (p + p^2)b/2$, *i.e.*, $P_2 = a - pb + (p - p^2)b/2$, where a and b are constants for each temperature. A comparison with equation (9) shows that, provided P_a be negligible (see below), $a = P_{E+A+O}$ and $b = A_{E+O}$, so that

$$P_2 = P_{E+A+O} - pA_{E+O} + \tfrac{1}{2}(p + p^2)A_{E+O} \quad . \quad . \quad . \quad (10)$$

The values of P_{E+A+O} and A_{E+O} calculated from Pal's data by means of equation (10), by using the method of zero sum, are given in Table I.

TABLE I.

Polarisation of nitrobenzene.

t.	$P_{E+A+O}(p = 0)$.	A_{E+O}.	$P_{E+A+O} - A_{E+O}(p = 1)$.
10°	440·2	385·6	54·6
20	427·6	373·7	53·9
30	416·2	362·9	53·3
40	405·0	352·3	52·7
50	395·0	342·4	52·6

The values of P_2 calculated from these data are compared in Table II with the experimental values at 10° : there is equally good agreement between the calculated and experimental values at the other temperatures, and these lie on a series of smooth curves, which are plotted in Fig. 1.

Comparison of equations (9) and (10) shows that K_2 for nitrobenzene must have the the value $\tfrac{1}{2}(p - p^2)A_{E+O}$. This means that the polarisation due to the association of liquid nitrobenzene vanishes when the volume polarisation is zero or unity, and in these limiting cases the polarisation formula for nitrobenzene reduces to the expression (4). Hence the dipole moment (μ) of nitrobenzene may be calculated by a method similar to that already used in the case of non-associating liquids, *viz.*, the temperature variation of the $p = 0$ intercepts given by equation (10), and these should vary in accordance with the Debye equation, $1·2732\sqrt{P_0 T} = \mu$.

Values for the $p = 0$ and $p = 1$ intercepts at several temperatures for nitrobenzene are given in Table I, and from these a graph has been compiled (Fig. 2) to compare, at 25°, all the data given by Pal (*loc. cit.*), Fairbrother (*loc. cit.*), and Jenkins (J., 1934, 480) for nitrobenzene in several different solvents. The values for carbon tetrachloride, hexane, and decane all lie on a curve represented by expression (10), those for benzene and p-xylene

TABLE II.

Nitrobenzene in carbon tetrachloride at 10°.

c_2.	$p.$*	P_2, found.*	P_2, calc.	c_2.	$p.$*	P_2, found.*	P_2, calc.	c_2.	$p.$*	P_2, found.*	P_2, calc.
—	0·0000	—	440·2	0·0959	0·5419	277·9	279·1	0·5917	0·8717	126·2	125·7
0·0099	0·3274	358·9	356·4	0·1527	0·6297	241·1	242·1	0·7166	0·8947	113·3	113·3
0·0210	0·3629	345·7	344·8	0·2098	0·6937	213·4	213·6	0·8046	0·9074	106·2	106·5
0·0319	0·3953	334·2	333·8	0·3103	0·7683	178·0	178·2	0·8936	0·9183	100·2	100·5
0·0469	0·4355	319·2	319·4	0·4039	0·8148	155·5	155·1	1·0000	0·9285	94·1	94·9
0·0706	0·4915	297·8	298·8	0·5001	0·8481	138·5	138·0	—	1·0000	—	54·6

* Pal (*loc. cit.*).

FIG. 2.

Nitrobenzene in solution at 25°.
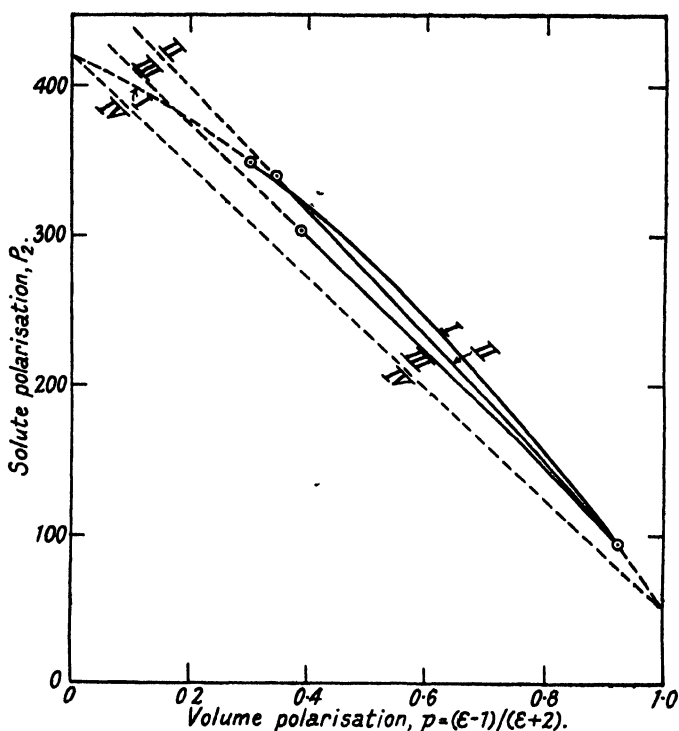
Curve.	Solvents.	Formula.
I	CCl$_4$, hexane, decane	$P_2 = P_{\mathrm{B+A+O}} - pA_{\mathrm{B+O}} + \frac{1}{2}(p + p^2)A_{\mathrm{B+O}}.$
II	Benzene, *p*-xylene	
III	CS$_2$,CHCl$_3$	$P_2 = P_{\mathrm{B+A+O}} - pA_{\mathrm{B+O}} + \frac{1}{2}(p + p^2)A_{\mathrm{B+O}} - K_1c_1/c_2.$
IV	?	$P_2 = P_{\mathrm{B+A+O}} - pA_{\mathrm{B+O}}$

on a curve of the type (9), and those for carbon disulphide and chloroform on a different curve of the same type corresponding to a high value of K_1. In order to calculate the moment, it appears preferable to employ the values given by Fairbrother for decane solutions which cover a wide temperature range, in conjunction with the $p = 1$ intercepts already obtained from Pal's data, which change but slightly with temperature (Table III). In this way a value of $4·28D$ is obtained, in close agreement with Groves and Sugden's value (J., 1934, 1094) for the vapour. It will be noted that, if the basis of these calculations is correct, the invariable term of the polarisation for nitrobenzene is 38·4 c.c., very little higher than Groves and Sugden's value for $P_{\mathrm{B+A}}$ in the vapour state, so that the term P_a is either zero or negligibly small.

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TABLE III.

Nitrobenzene in decane.

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$t.$	$p.$*	$P_{\text{E}+\text{A}+\text{O}} - A_{\text{E}+\text{O}}.†$	$P_2.$*	$P_{\text{E}+\text{A}+\text{O}}.$	$t.$	$p.$*	$P_{\text{E}+\text{A}+\text{O}} - A_{\text{E}+\text{O}}.†$	$P_2.$*	$P_{\text{E}+\text{A}+\text{O}}.$
20°	0·3186	53·9	345·2	423·4	80°	0·2891	51·8	301·1	358·2
40	0·3084	52·8	329·2	399·1	100	0·2797	51·8	289·0	340·7
60	0·2986	52·1	314·2	377·2	120	0·2708	51·8	278·5	325·6

<div align="center">

$\mu = 4·28D$; $P_{\text{E}+\text{A}} = 38·4$ c.c.; $P_{\text{E}} = 32·0$ c.c.

* Fairbrother (*loc. cit.*).   † See Table I.

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An important conclusion to be drawn from expression (9) is that, in selecting data for the calculation of dipole moments, either of associating or of non-associating substances, the solvents must be such as carbon tetrachloride or the paraffin hydrocarbons, giving a zero value for K_1; this should replace the older conception that such solvents should be merely non-polar, and any confusion on this point is seen to be particularly misleading in the case of the aromatic hydrocarbons.

It will be noticed that the curves for *n*-butyl alcohol, calculated from the data of Smyth and Stoops (*loc. cit.*) and plotted in Fig. 1, are more complex than those for nitrobenzene; it is evident that K_2 for the alcohols must be a more complex function of p than it is in the case of nitrobenzene.

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SUMMARY.

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1. The differences observed between the dielectric polarisation of liquids and gases are attributed mainly to decreases due to the anisotropy and the association of the solvent, and to an increase due to the association of the solute.

2. A formula for the polarisation of liquids is deduced and exemplified by reference to the behaviour of nitrobenzene in various solvents.

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114. *The Vapour-pressure Curve of Formaldehyde, and Some Related Data.*

By ROBERT SPENCE and WILLIAM WILD.

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A NUMBER of measurements of the vapour pressure of formaldehyde have already been reported by Mali and Ghosh (*J. Indian Chem. Soc.*, 1924, **1**, 37). Their specimen polymerised rapidly above $-30°$ but was sufficiently stable at lower temperatures to allow five determinations to be made between $-91°$ and $-34·5°$. However, these points are insufficient for the accurate determination of the curve. Accordingly, a new series of measurements has been carried out with relatively stable specimens (cf. Spence and Wild, this vol., p. 338).

Liquid formaldehyde, prepared from paraformaldehyde (*idem, ibid.*), was distilled, the head and tail fractions being discarded. The condensate was redistilled, and about 2 ml. of the middle fraction collected in the vapour-pressure vessel, which was then sealed off. All condensing surfaces had previously been heated in the presence of formaldehyde vapour. The cylindrical vapour-pressure vessel was surrounded by a brass tube carrying the copper wire of a resistance thermometer, and the whole immersed in a 3-litre Dewar flask filled with ligroin (b. p. 40—60°) at the desired temperature. A U-tube containing pure redistilled α-bromonaphthalene separated the formaldehyde vessel from the manometric system, but the former could be pumped out by opening a stop-cock placed across the limbs of the U. All exposed tubing except the portion containing bromonaphthalene was maintained at 100°.

Measurement of Temperature.—The resistance of the thermometer was measured on a Pye dial resistance box. With the galvanometer used, measurements were accurate to 0·01 ohm. For purposes of calibration, the copper thermometer was immersed in ligroin (b. p. 40—60°) in a large Pyrex test-tube. Four fixed points were determined, *viz.*, the transition point of sodium sulphate decahydrate (32·38°; Landolt–Börnstein, " Tabellen "), the m. p. of ice, the transition

point of carbon tetrachloride (— 47·66°; Johnston and Long, *J. Amer. Chem. Soc.*, 1934; **56**, 31), and the sublimation point of solid carbon dioxide (— 78·5°; Landolt–Börnstein, " Tabellen ") : all these materials had been carefully purified before use. The variation of resistance with temperature could be represented by the empirical equation $R_t = 72 \cdot 01 + 0 \cdot 30506t - 73 \times 10^{-6}t^2$. Resistances calculated from this equation are here compared with the experimental values :

$t°$	$32 \cdot 38°$	$0 \cdot 00°$	$-47 \cdot 66°$	$-78 \cdot 50°$
$R_{obs.}$, ohms	81·89	72·01	57·35	47·59
$R_{calc.}$, ohms	81·81	72·01	57·31	47·61

During the vapour-pressure measurements, the ligroin bath was stirred by a stream of dry air. With a properly regulated rate of flow, the bath temperature remained constant to within 0·05° for the period of a determination.

Measurement of Pressure.—The apparatus was first thoroughly evacuated by a mercury-diffusion pump, the stop-cock connecting the two limbs of the U-tube closed, and the formaldehyde bulb, together with the thermometer, immersed in the ligroin bath at the desired temperature. Pressures less than 10 mm. of mercury were measured directly by using the bromonaphthalene U-tube as a differential manometer. At higher pressures, the differential manometer was approximately balanced by admission of dry air to the evacuated limb. Balancing pressures up to 86·00 mm. of mercury were measured on a bromonaphthalene manometer, whilst mercury was used for the higher values. The reading on the differential manometer was added to or subtracted from the balancing pressure according to whether the vapour pressure was greater or less than the latter. Data given in the table below (p in mm. of Hg) represent the average of three or four settings.

Attainment of the maximum vapour-pressure was rapid, but in a few cases a slow drift occurred owing to increasing bath temperature. On the other hand, solution and polymerisation in the bromonaphthalene U-tube were shown to be negligibly small by the fact that the pressure of formaldehyde confined over bromonaphthalene decreased only very slowly. Again, the b. p. obtained from the vapour-pressure curve has been checked by direct determination.

Vapour-pressure of formaldehyde.

Sample.	t.	p, obs.	p, calc.	Diff.	Diff., %.	Sample.	t.	p, obs.	p, calc.	Diff.	Diff., %.
B1	— 109·4°	0·95	1·03	—0·08	7·8	A4	— 64·6°	61·65	61·87	—0·22	0·4
C2	— 104·4	1·85	1·83	+0·02	1·1	A6	— 63·7	65·20	65·65	—0·45	0·7
C1	— 98·3	3·60	3·54	+0·06	1·7	C7	— 55·8	111·0	110·7	+0·3	0·3
A11	— 95·2	4·85	4·83	+0·02	0·4	A2	— 54·0	124·7	123·7	+1·0	0·8
A12, C3	— 89·1	8·68	8·68	0·00	0·0	A7	— 49·3	163·1	164·5	—1·4	0·7
C4	— 85·6	12·25	11·96	+0·29	2·4	A8	— 40·6	266·6	268·0	—1·4	0·5
A5	— 78·9	21·02	20·97	+0·05	0·2	C8	— 39·1	290·6	290·6	0·0	0·0
C5	— 78·3	22·11	22·02	+0·09	0·4	A1	— 34·3	368·9	372·6	—3·7	1·0
A10	— 71·9	35·40	36·30	—0·90	2·5	A9	— 28·4	496·6	498·8	—2·2	0·4
C6	— 68·5	46·43	46·91	—0·48	1·0	C9	— 22·3	664·3	661·3	+3·0	0·5
A3	— 65·3	58·95	58·74	+0·21	0·4						

The calculated pressures have been obtained from the following empirical equation :

$$\log_{10}p_{atm.} = -1429/T + 1 \cdot 75 \log T - 0 \cdot 0063T + 3 \cdot 0177,$$

where T represents degrees absolute. The deviation is usually not more than 1%, the average being 1·1%. Four samples of liquid monomeride were used. In the first case, temperature was measured with a pentane thermometer. These results are not shown, but agree very closely with those given in the table. The three remaining samples are represented in col. 1 by A, B, and C, with serial numbers showing the order of the experiment. In Fig. 1, the line represents the above relation between log p and $1/T$, but with p in mm., and the positions of the experimental points are shown.

Melting Point and Boiling Point.—Pure redistilled formaldehyde was condensed in a tube (10 mm. diameter) containing a large glass bead. The tube was sealed off and suspended in a 3-l. ligroin bath in an inverted sloping position. At the m. p. the bead fell to the bottom, so bringing the tube vertical and making an electrical connexion causing a bell to ring. This occurred at — 118·3°. The range of melting was now investigated. Formaldehyde was frozen in the bottom of a tube (10 mm. diameter) of the type shown in Fig. 2(a). This contained a glass weight with a long pointer attached, which was hooked to the tube by a small projection

near the top. When sufficient formaldehyde had collected, the tube was sealed off above the pointer, the hook of which was then released by tapping, and the weight allowed to rest on the surface of the solid. The tube was placed in the 3-l. ligroin bath so that the tip of the pointer protruded about 1 cm. above the mouth of the Dewar flask. Downward movement first became visible at $- 118\cdot3°$ and the pointer reached the bottom mark at $- 117\cdot6°$. Such a range of melting appeared to be unduly large. Accordingly, another experiment was performed with an m. p. tube only 6 mm. in diameter and with very careful regulation of the bath temperature. The range of melting as indicated by the pointer was now $- 118\cdot3°$ to $- 117\cdot8°$. The vapour pressure calculated from the equation is $0\cdot35$ mm. at the m. p. Boiling-point determinations were carried out (a) by Smith and Menzies's bulblet method (*J. Amer. Chem. Soc.*, 1910, **32**, 897), and (b) by their isoteniscope method (*ibid.*, p. 1420). The simple form of isoteniscope used is shown in Fig. 2(b). Formaldehyde was condensed in the single limb and in the U by liquid air, and the apparatus sealed off from the main train at A. The wide upper tube was now held by a clamp and the lower portion immersed in a ligroin-bath just above the b. p. When the formaldehyde in the U melted, the capillary tip of the wide tube was broken, admitting air. Formaldehyde vapour bubbled through the liquid in the U. The bath temperature was now gradually

FIG. 1.

FIG. 2.

(a)   (b)
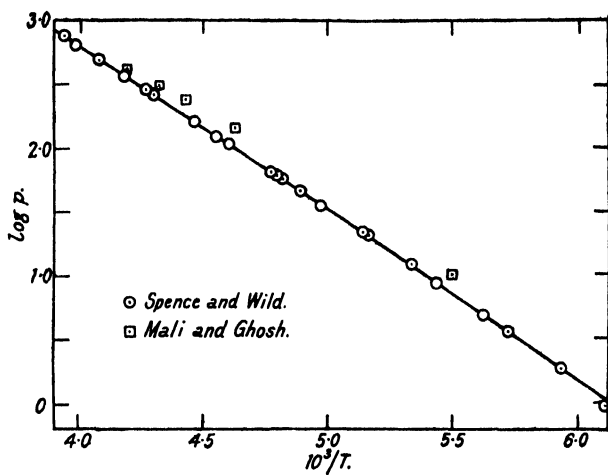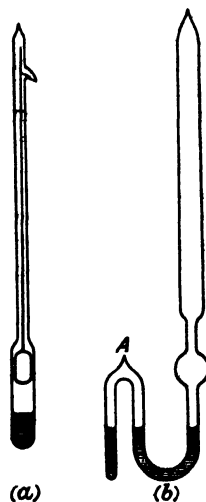
lowered by addition of solid carbon dioxide until bubbling ceased and the levels in the U became the same. Measurement of three different samples by method (a) gave $- 19\cdot3°$, and the mean of six readings by method (b) with one sample was $- 19\cdot3°$, corrected to 760 mm. The b. p. calculated from the vapour-pressure equation is $- 19\cdot1°$, whence the mean of the direct and the indirect determinations is $- 19\cdot2°$. Attempts were made to determine the critical temperature of formaldehyde by placing a sealed capillary tube containing the liquid in an oil-bath at a definite temperature. Precise observations were impossible owing to the occurrence of rapid polymerisation. At 147° the liquid expanded and almost filled the tube. As the temperature rose, solid at first separated, but this eventually melted, and the contents of the tube appeared to remain unchanged until the latter burst at 250°.

Thermodynamic Constants.—Differentiation of the above vapour-pressure equation, and combination of the result with the simplified Clausius–Clapeyron equation : $d \log_e p/dT = \Delta H/RT^2$, leads to the following expression for the heat of vaporisation : $\Delta H = 6545 + 3\cdot480T - 0\cdot02885T^2$. At the b. p., $- 19\cdot2°$ ($253\cdot9°$ K.), $\Delta H = 5570$ cals. The value of Trouton's constant, $\Delta H/T$, is $21\cdot9$ entropy units.

DISCUSSION.

The results of Mali and Ghosh (Fig. 1) show considerable deviation from the curve derived from our table. This may be due to an error in their thermocouple, which was checked only at a single temperature. Furthermore, the b. p. is given as $- 21°$, identical with Kekulé's figure (*Ber.*, 1892, **25**, 2435), but the value calculated from their equation is

— 20°. The accuracy of our results appears to be limited chiefly by temperature variation, and it is probable that the difference of 0·2° between the b. p. measured at atmospheric pressure and that calculated from the vapour-pressure equation lies within the limits of experimental error. The results were not considered to be sufficiently accurate to justify correction for the local value of g and for the expansion of mercury (cf. Smith and Menzies, *loc. cit.*). It is evident from the vapour-pressure data and from the value of Trouton's constant, that formaldehyde is a normal liquid. Actually, however, certain measurements (*e.g.*, A12 and C9) were carried out with specimens which had become gelatinous, without any apparent deviation from the curve. Furthermore, the fact that no deviation occurred when fresh specimens were employed initially at widely different temperatures demonstrates the uniform purity of the liquid phase. It must be concluded, therefore, that the polymerisation of monomeric liquid formaldehyde, like that of the gas, occurs only at the surface of the solid polymeride, which is insoluble and possesses negligible vapour pressure. The insolubility of the polyoxymethylene in monomeric formaldehyde is remarkable, although in agreement with the very high molecular weight now attributed to it. The process of gelatinisation probably occurs as follows. Thread-like molecules of polyoxymethylene grow out from the glass walls or from suspended matter into the liquid. As the threads thicken, they become visible locally as faint, woolly formations, which gradually extend until there is a semi-rigid network which retains a relatively large mass of unchanged liquid. The enclosed liquid behaves as if it is entirely pure, and exerts its normal vapour pressure.

SUMMARY.

The vapour-pressure curve of formaldehyde has been traced from the m. p. (− 118·0°) to the b. p. (− 19·2°).

The heat of vaporisation is 5570 cals. at the b. p., and Trouton's constant is 21·9 entropy units, whence it is concluded that formaldehyde is a normal liquid.

Polymerisation occurs only as a heterogeneous or solid phase reaction, leaving the liquid phase unaffected.

115. *Absorption Spectra of Polycyclic Hydrocarbons. Part I. Alkyl-substituted Phenanthrenes.*

By F. A. ASKEW.

THE ultra-violet absorption spectra of a number of compounds related to phenanthrene have been determined, in view of their bearing on the structure of the sterols, and, more directly, on the " Diels hydrocarbon " $C_{18}H_{16}$. The absorption spectra of this compound and of synthetic 1 : 2-*cyclo*pentenophenanthrene and its 3′-methyl derivative have already been reported (Harper, Kon, and Ruzicka, J., 1934, 124 ; see also Cook and Hewett, J., 1933, 1103), and those of a series of 18 alkyl-substituted phenanthrenes are now described, and their relationships to the *cyclo*-compounds discussed. Further data on partly reduced compounds of this series are in the following paper.

Methods and Units.—Alcoholic solutions of the substances were photographed in a quartz cell, a hydrogen-discharge tube being used as a source of continuous ultra-violet radiation. The technique and apparatus used in the spectrography and in measuring the extinction coefficients were as described by Philpot and Schuster (Medical Research Council, Spec. Report Series, No. 177).

The figures are plotted with wave-lengths as abscissæ and values of log ε/c as ordinates, where ε is the extinction coefficient and c the concentration in g.-mols. per litre. The latter units have been used in order to render the results more easily comparable with those of other workers, although in previous papers from this laboratory, concentrations have been expressed in g. per litre.

The table gives the values for log ε/c for the maxima and minima of the bands observed in the series of alkyl-substituted phenanthrenes, together with the values for phenanthrene (Clar,

(In each case, the upper row gives λ, in mμ, and the lower log ε/c.)

	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max
Phenanthrene.	345	342	337	334	329	326	322	319	314	308	293	287	282	278	275	271	251
	2·44	1·70	2·36	1·80	2·46	2·16	2·34	2·15	2·32	2·19	4·10	3·66	3·99	3·97	4·10	4·07	4·70
9-Methyl	349	344	340	337	331	330	325	322	317	314	297	290	284	281	277	273	252
	2·64	2·15	2·41	2·32	2·63	2·37	2·45	2·38	2·49	2·44	4·07	3·77	3·99	3·98	4·13	4·14	4·79
1-Ethyl	349	346	341	337	333	330	326	322	318	314	300	293	288	283	277	273	256
	2·46	2·04	2·32	2·23	2·52	2·30	2·36	2·28	2·42	2·35	4·12	3·75	4·01	3·86	4·03	3·96	4·70
1 : 2-Dimethyl	350	348	343	340	335	330	328	324	320	314	300	295	288	285	279	274	258
	2·43	2·08	2·29	2·26	2·58	2·36	2·37	2·35	2·49	2·38	4·11	3·79	4·02	3·84	4·20	4·14	4·81
1 : 3 „	350	348	344	340	335	330	329	324	320	317	300	297	290	286	279	277	258
	2·66	2·20	2·40	2·34	2·67	2·40	2·44	2·37	2·56	2·52	4·10	3·83	4·02	3·86	4·03	3·99	4·69
1 : 7 „	351	348	341	339	335	330	326	324	320	314	301	295	289	286	280	276	259
	2·30	2·09	2·34	2·32	2·55	2·38	2·40	2·35	2·51	2·42	4·16	3·75	4·04	3·96	4·14	4·07	4·84
1 : 8 „	351	348	344	340	335	331	330	~	~	~	306	298	292	288	281	278	259
	2·35	2·14	2·40	2·37	2·54	2·46	2·51				4·23	3·84	4·14	3·86	4·04	3·94	4·76
1 : 9 „	351	348	344	340	335	331	328	326	320	316	303	296	290	286	280	275	258
	2·68	2·24	2·40	2·39	2·69	2·42	2·45	2·43	2·58	2·55	4·17	3·92	4·13	4·03	4·17	4·11	4·76
2 : 3 „	349	347	340	337	332	330	326	321	317	313	297	292	285	~	279	276	254
	2·23	2·04	2·27	2·23	2·41	2·33	2·56	2·36	2·45	2·44	4·00	3·60	3·95		4·06	4·03	4·68
2 : 5 „	350	346	344	~	333	~	328	324	319	314	298	292	287	283	277	273	253
	2·19	2·02	2·20	~	2·45	~	2·31	2·28	2·35	2·30	4·05	3·73	3·95	3·88	4·05	3·99	4·83
4 : 9 „	350	345	~	~	334	~	~	326	320	317	299	294	289	283	277	273	253
	2·74	2·43	~	~	2·74	~	~	2·47	2·56	2·54	4·06	3·90	4·00	3·93	4·03	4·01	4·84
7-Methyl-1-ethyl	349	347	~	~	334	329	326	323	319	314	300	295	287	284	279	274	258
	2·19	1·98	~	~	2·48	2·30	2·33	2·31	2·47	2·38	4·29	3·77	4·05	3·99	4·15	4·10	4·82
1 : 2 : 7-Trimethyl	353	348	~	~	337	~	~	326	322	317	302	298	291	288	283	278	260
	2·60	2·26	~	~	2·71	~	~	2·42	2·60	2·46	4·10	3·74	4·08	4·06	4·18	4·14	4·82
1 : 3 : 7 „	352	349	344	340	337	333	330	326	319	317	304	297	290	288	281	278	260
	2·21	2·09	2·31	2·30	2·49	2·36	2·40	2·34	2·55	2·54	4·13	3·82	4·02	3·96	4·14	4·11	4·78
1 : 4 : 7 „	354	349	~	~	337	334	332	329	323	~	307	300	295	288	282	279	257
	2·53	2·34	~	~	2·64	2·51	2·53	2·51	~		4·14	3·94	4·06	3·90	4·00	3·98	4·82
1 : 6 : 7 „	351	348	343	340	335	~	~	324	320	315	302	295	290	286	281		258
	2·73	2·53	2·63	2·60	2·78	~	~	2·52	2·66	2·56	4·17	3·77	4·02	3·93	4·12	4·06	4·83
1 : 2 : 8 „	354	351	347	~	339	332	—	—	323	320	307	301	295	290	283	280	261
	2·18	2·15	2·30	~	2·54	2·41	—	—	2·62	2·61	4·19	3·84	4·08	3·89	4·07	3·99	4·77
1-Methyl-7-*iso*propyl	351	348	344	~	334	330	~	~	318	314	301	294	288	285	279	275	259
	2·36	2·18		~	2·58	2·46	~	~	2·80	2·75	4·19	3·88	4·11	4·04	4·20	4·11	4·85
1-Ethyl-7-*iso*propyl	350	~	340	~	333	330	328	323	318	314	300	297	288	286	280	276	258
	2·05	~	2·30	~	2·51	2·33	2·36	2·32	2·47	2·41	4·16	3·65	4·06	4·02	4·18	4·15	4·83

Ber., 1932, **65**, 846). The full curves for 1 : 2-dimethyl- and 1 : 2 : 8-trimethylphenanthrene and 1 : 2-*cyclo*pentenophenanthrene are given in the fig.

All the curves showed the same general form as the spectrum of phenanthrene, *viz.*, a series of five bands between 300 and 355 mμ, a series of three bands of considerably greater intensity between 270 and 300 mμ, and a still more intense maximum at about 250 mμ.

In the table, similar bands are grouped in the same vertical column; in some cases no definite values could be ascribed to the maxima or minima, though a marked inflexion was apparent in the curve; such cases are denoted in the table by the sign ~.

Additional bands. Besides the maxima and minima tabulated, the following bands (in mμ) were observed :

```
        1 : 7-Dimethylphenanthrene ..........................   381    371    359
        2 : 3-Dimethylphenanthrene ..........................   379           358    311
        1 : 6 : 7-Trimethylphenanthrene    ..........................   380           360
```

These bands do not appear to be due to the alkylphenanthrenes themselves, but rather to some absorbing impurity, since they were produced to varying extents by different specimens of the same compound. They were still obtained, however, with the purest available samples of these compounds. Again, if these bands were characteristic of some particular grouping (*e.g.*, 1 : 7, or 2 : 3 which is equivalent to 6 : 7), one would expect similar bands to be produced by analogous compounds such as 7-methyl-1-ethylphenanthrene; this does not occur. It does not appear that a common impurity was introduced by a common method of synthesis, since a specimen of 1 : 7-dimethylphenanthrene prepared from *d*-pimaric acid still showed the extra bands. It is more probable that these bands are due to products of decomposition. The spectra of these

compounds are included in the table, since these extra bands mostly occurred in regions outside the ordinary phenanthrene spectrum, and variations in their height between different specimens did not greatly affect the other bands.

The structure of 4 : 9-dimethylphenanthrene is less well established than those of the other compounds described.

The data given in the table lead to the following tentative conclusions :

(1) No additional complication appears to be introduced into the spectrum of phenanthrene when the symmetry of the molecule is destroyed by the introduction of alkyl groups: phenanthrene and its 1 : 8-dimethyl homologue are symmetrical, but have as many bands (or inflexions) as the others.

(2) Although the wave-lengths of the maxima vary from one compound to another, there is a general shift towards the longer wave-lengths as the number of substituent alkyl
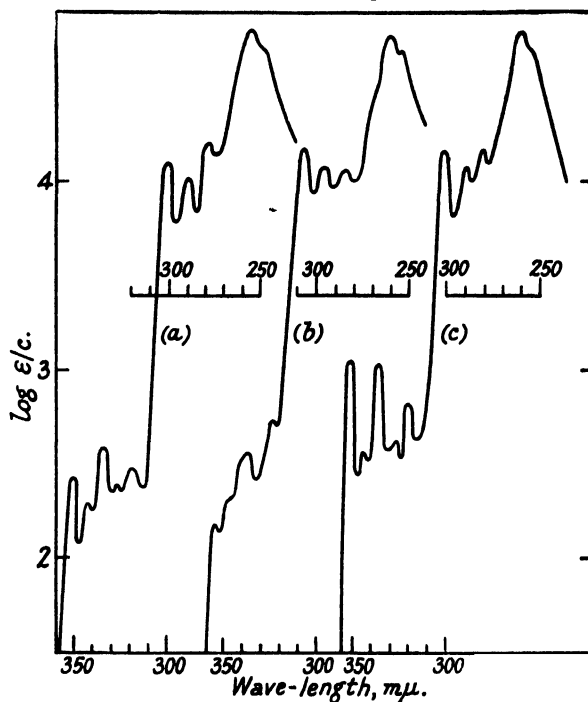
(a) 1 : 2-*Dimethylphenanthrene.*
(b) 1 : 2 : 8-*Trimethylphenanthrene.*
(c) 1 : 2-cyclo*Pentenophenanthrene.*

groups increases, and the distinctness of the maxima and minima tends to become less marked ; many of the maxima and minima present in the simpler compounds merge into inflexions in the series of tri-substituted compounds (cf. 1 : 2-dimethyl- and 1 : 2 : 8-trimethyl-phenanthrenes). Both these effects are in accordance with observations of de Laszlo (*Z. physikal. Chem.*, 1925, **118**, 369) on mono- and di-methylnaphthalenes, and of Radulescu and Ostrogovitch on β-methylanthracene (*Ber.*, 1931, **64**, 2233).

(3) The data in the table would seem to indicate that the wave-length shift depends on the number rather than on the size of the substituents.

(4) Within the series of dimethyl-substituted compounds, the maxima of those with a substituent in the 1-position tend to be at longer wave-lengths than those without.

(5) In contrast to the smoothing-out effect of increasing number of alkyl substituents, mentioned in (2) above, the effect of the fusion to the phenanthrene nucleus of a poly-methylene or other saturated ring appears to be a marked increase in the heights of the first and the third maximum (at about 350 mμ and 335 mμ) compared with the corresponding dialkyl compound. This effect can be seen in the fig. (curves *a* and *c*). Similarly

high maxima are shown by 3'-methyl-1 : 2-*cyclo*pentenophenanthrene (Harper, Kon, and Ruzicka, *loc. cit.*), and a similar effect is to be seen by comparison of the curves of 6 : 7-*cyclo*penteno- and 6 : 7-dimethyl-1 : 2-benzanthracene (Rosenheim and King, *J. Soc. Chem. Ind.*, 1933, **52**, 299) and also in 1 : 10-trimethylenephenanthrene and in several other compounds containing a phenanthrene-ring system having a saturated ring fused on (see Clar, *Ber.*, 1933, **66**, 202, Figs. 3, 4, 5, 6).

(6) It will be seen from the table that the greatest variation in the heights of the maxima takes place in the region 300—350 mμ. According to Clar (*Ber.*, 1932, **65**, 1411), these bands in the phenanthrene spectrum are due to the " diyl " states of the molecule :
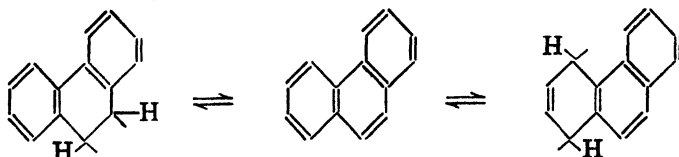
If these views are correct, the variations in these bands in the present series of compounds should be connected with the effect of substituents on the capacity of the molecule to assume the " diyl" state. Clar (*Ber.*, 1933, **66**, 202) has attempted to correlate the first, third, and fifth bands (at 345, 329, and 314 mμ in phenanthrene) with the 9 : 10- " diyl" state and the second and fourth (at 337 and 322 mμ) with the 1 : 4-" diyl " state.

From the table it may be seen that the compounds having a substituent in the 9 (or 10) position have considerably higher values of log ε/c for the first, third, and fifth maxima than have the other members of the series. On the other hand, there does not appear to be any direct correlation between the second and fourth maxima and the presence or absence of substituents on the 1 : 4 (or 5 : 8) carbon atoms.

The author's thanks are due to Dr. R. D. Haworth for kindly supplying purified samples of alkylphenanthrenes synthesised by him and his co-workers, to Dr. O. Rosenheim for helpful advice and criticism, to his colleagues Dr. R. K. Callow and Mr. J. St. L. Philpot, and also to Mr. E. H. Pitte, for assistance at various times with the measurements.

116. *Absorption Spectra of Polycyclic Hydrocarbons. Part II. Partially Reduced Derivatives of Phenanthrene, etc.*

By F. A. ASKEW.

THE ultra-violet absorption spectra of compounds of this series were measured with the object of elucidating the relationship between the absorption spectra and the positions of double bonds in compounds of the sterol group.

The compounds measured include 9 : 10-dihydrophenanthrene, tetrahydrophenanthrene, and two isomeric octahydrophenanthrenes, together with *cis*- and *trans*-hexahydrochrysene, 7 : 8-dihydrophenalyl-7-*spirocyclo*pentane, and fluorene. Relationships between the spectra of these compounds and those described in Part I (preceding paper) are discussed below, together with the bearing of some of the results on Clar's theory (*Ber.*, 1932, **65**, 503, 846, 1411) regarding the correlation between certain parts of the spectrum and the " diyl " state.

The methods and units employed were as described in Part I.

9 : 10-*Dihydrophenanthrene* (I).—A specimen of this compound, prepared from phenanthrene by catalytic reduction (Schroeter, Müller, and Huang, *Ber.*, 1929, **62**, 645), m. p. 35°, gave the absorption spectrum reproduced in Fig. 1. Comparison with that of phenanthrene (II and IIa) (Clar, *loc. cit.*, p. 846) shows that saturation of the 9 : 10 double bond is accompanied by considerable changes; the series of sharp bands between 300 and 350 mμ has entirely disappeared, the

bands about 290 mμ have become less marked, and the main band has been displaced towards the longer wave-lengths.

This observation, together with others (p. 516), accords well with Clar's hypothesis regarding the connexion between absorption spectra and the reactive "diyl" state of condensed poly-nuclear hydrocarbons. According to his views, phenanthrene (II), for example, exists in equili-

FIG. 1.

FIG. 2a.   FIG. 2b.

———— 1 : 2 : 3 : 4-*Tetrahydro-*   7 : 8-*Dihydrophenalyl-7-*
          phenanthrene   spirocyclo*pentane.*
     (*Two samples,* A *and* B).
– – – – *Naphthalene.*

———— 9 : 10-*Dihydrophenanthrene.*
– – – – *Phenanthrene.*
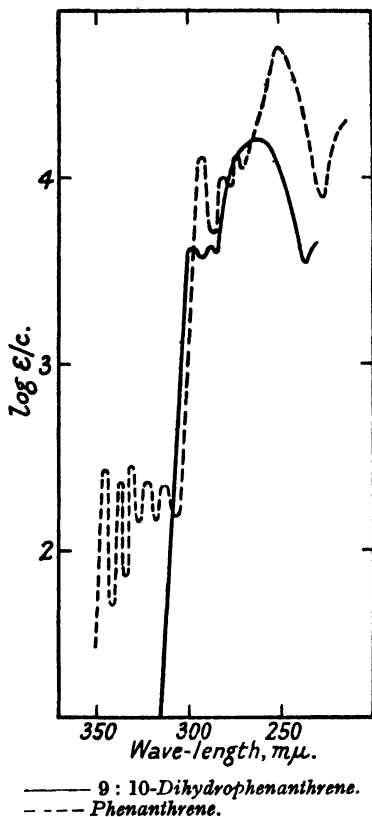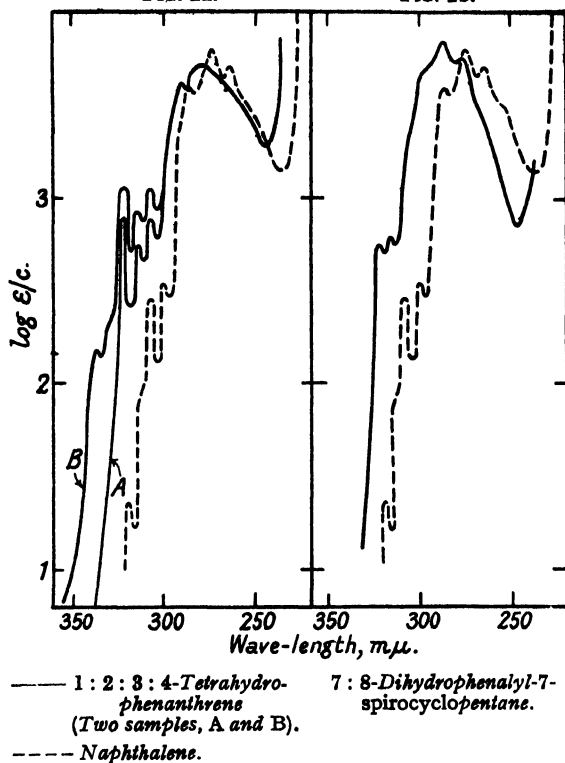
brium with a reactive form (IIa) to which many of its properties are due, and the series of sharp bands in its spectrum between 300 and 350 mμ is due to the presence of such a reactive form.

(I.)   (II.)   (IIa.)   (III.)
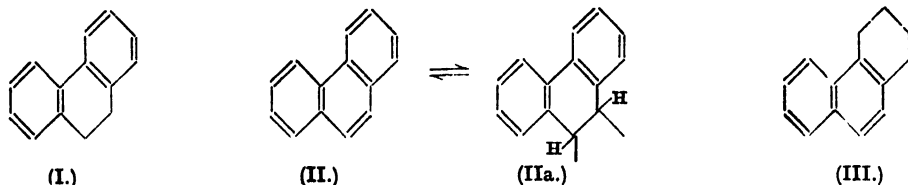
The fact that the bands attributed to the " diyl " state have completely disappeared in 9 : 10-dihydrophenanthrene affords experimental confirmation of Clar's correlation between these bands and such 9 : 10-reactivity.

1 : 2 : 3 : 4-*Tetrahydrophenanthrene* (III).—The spectra of two specimens from different sources are shown in Fig. 2a. One specimen (A) was prepared by catalytic reduction of phenanthrene (Schroeter, Müller and Huang, *loc. cit.*), the other (B) by Clemmensen reduction of 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene. The spectra practically coincide over the region 250—300 mμ, and the bands at 307, 313, and 321 mμ are similar in form and wave-length, but differ in height, and specimen B shows an extra band at 336 mμ. This difference suggests the presence of an impurity absorbing at these wave-lengths. Since specimens A and B were prepared by different methods,

it seems possible that this impurity is a product of decomposition (both specimens rapidly turned yellow on keeping) and that, in general form, the spectrum is that of tetrahydrophenanthrene.

7 : 8-*Dihydrophenalyl*-7-spirocyclo*pentane* (IV).—A specimen of this compound, prepared by the method of Cook and Hewett (J., 1933, 1098; 1934, 365), gave the spectrum shown in Fig. 2b. Comparison of the spectra of (III) and (IV) with that of naphthalene (reproduced from Clar and Lombardi, *loc. cit.*) shows a considerable resemblance between these three compounds. The curves are of similar form, but that of tetrahydrophenanthrene is displaced from that of naph- thalene towards the longer wave-lengths by about 7 mμ, while that of the *spiro*-compound (IV) is displaced by about 15 mμ. The maxima of both these compounds are less well marked than those of naphthalene. These effects are in accordance with the structures of these compounds, since they can both be regarded, from the point of view of absorption spectra, as alkyl-substituted

| FIG. 3a. | FIG. 3b. | FIG. 3c. |

Wave-length, mμ.

— 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12- ——— cis- ⎫ 1 : 2 : 9 : 10 : 11 : 18- ——— *Dodecahydrochrysene.*
Octahydrophenanthrene. ⎬ *Hexahydrochrysene.* - - - - *Dodecahydrotriphenyl-*
- - - 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8- - - - - trans- ⎭ *ene.*
Octahydrophenanthrene.
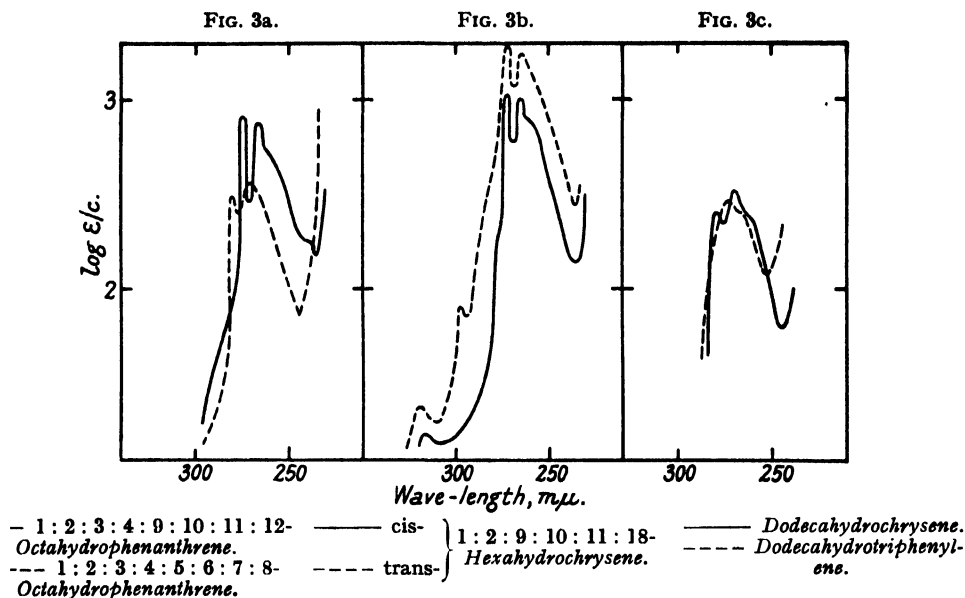
naphthalenes, which exhibit similar displacements and smoothing-out of maxima (de Laszlo, *Z. physikal. Chem.*, 1925, **118**, 369).

(IV.) (V.) (VI.) (VII.)

(VIII.) (IX.) (X.) (XI.)
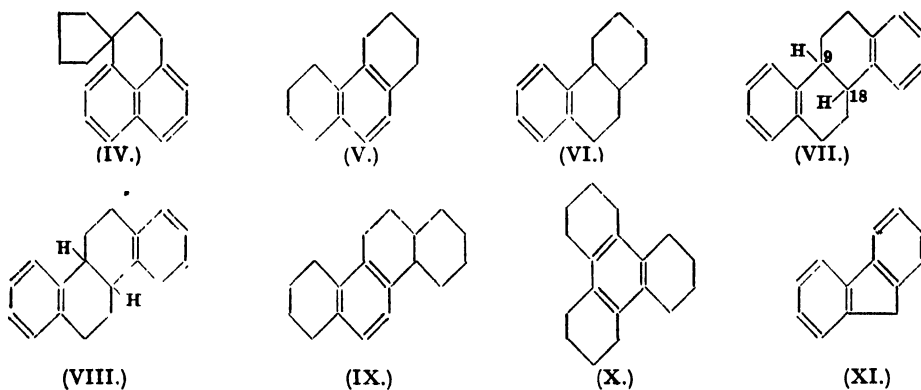
1 : 2 : 3 : 4 : 5 : 6 : 7 : 8- *and* 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydrophenanthrene* (V and VI).—A specimen of the symmetrical compound (V), prepared by catalytic reduction of phenanthrene (Schroeter, Hulle and Müller, *Ber.*, 1924, **57**, 2025), gave the spectrum reproduced in Fig. 3a, *viz.*, a main band having a maximum at 269 mμ and a second smaller maximum at 279 mμ.

The compound (VI), prepared by cyclisation at — 5° of 1-β-phenylethyl*cyclo*hexanol (Cook and Hewett, *loc. cit.*), gave the spectrum also reproduced in Fig. 3a. A measurement of another

specimen, prepared by cyclisation at 100° of 1-β-phenylethyl*cyclo*hexene (*idem, ibid.*), revealed the presence of a considerable proportion of tetrahydrophenanthrene, the formation of which is easily explained by the simultaneous dehydrogenation ensuing when the cyclisation is carried out at 100° (Dr. Cook, private communication). The presence of this impurity caused little change in the chemical properties, but produced a profound alteration in the spectrum.

The spectra of both the octahydrophenanthrenes are of the general type shown by benzene and its alkyl derivatives, as would be expected from the fact that each contains one substituted benzene ring. The spectra, however, differ considerably both in the wave-lengths of the maxima and in the relative heights of the maxima and minima; these differences are discussed below.

Fig. 4.   Fig. 5.

Wave-length, mμ.   *Wave-length, mμ.*

Fluorene.   *Fluorene*
———— *Menczel.*   (*purified specimen*).
– – – – "*Pure*" *fluorene, Spec.* A.
- - - - - „   „   „   B.
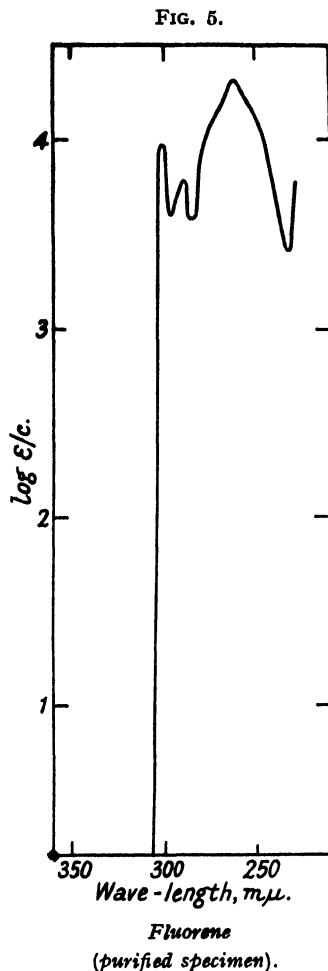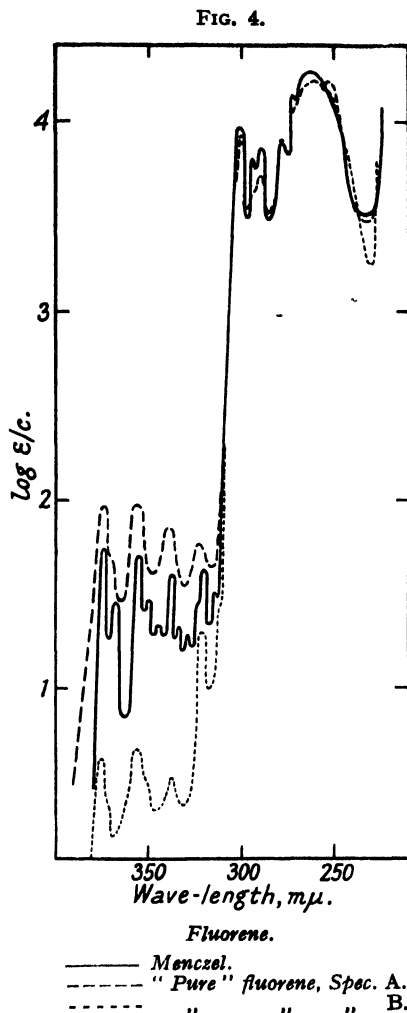
cis- *and* trans-1 : 2 : 9·10 : 11 : 18-*Hexahydrochrysene* (VII and VIII).—The spectra of specimens of these two compounds (Ramage and Robinson, J., 1933, 608), in which the *cis–trans*-isomerism is about the 9 : 18 bond, are shown in Fig. 3b. Apart from a difference in height, the two absorption spectra are similar. The reason for this may be that the important absorbing groups, the benzenoid rings, are some distance away from the centre of isomerism. In contrast to this similarity in spectra, Bernal (*Chem. and Ind.*, 1933, **52**, 287) found that the crystal structures of these two compounds were markedly different, the unit cell of the *cis*-form having 64 molecules, as against 2 for the *trans*-form. In Fig. 3c are shown the spectra of dodecahydrochrysene (Philpot, private communication) (IX) and dodecahydrotriphenylene (X) (Clar and Lombardi, *loc. cit.*).

Comparison of these spectra and the structures shows that those compounds with more than

one reduced ring fused to the benzenoid ring (compounds V, IX, X) show spectra having a maximum near 270 mμ, with a shoulder or small maximum near 280 mμ. On the other hand, compounds in which the benzenoid rings are in the end positions (compounds VI, VII, VIII) have two much sharper maxima at about 265 and 275 mμ, with a pronounced minimum between them.

Fluorene (XI).—As has been seen above, in dihydrophenanthrene, where the 9 : 10 double bond is reduced, the bands in the spectrum of phenanthrene attributed by Clar to the "diyl" state are no longer present. This being so, one would not expect such bands to be present in the spectrum of fluorene (XI). In Fig. 4 is shown Menczel's curve (*Z. physikal. Chem.*, 1927, **125**, 161) for the absorption spectrum of fluorene; it possesses a number of prominent bands between 300 and 375 mμ, *i.e.*, in the "diyl" region. Measurement of the absorption of two commercial specimens (A and B) of "pure" fluorene gave the results also shown in Fig. 4. Although the three curves agree fairly closely over the region 240—300 mμ, there is considerable divergence over the region 300—375 mμ, and one of the specimens (B) has a considerably lower absorption (intensity about 1/12) over this region than Menczel's specimen. The simplest explanation of this discrepancy is that all three samples contained different amounts of an impurity with a large absorption between 300 and 375 mμ. Capper and Marsh (J., 1926, 724) drew a similar conclusion, but their paper appears to have been overlooked by Menczel; their purest fluorene had only one small band in this region, at 319 mμ, but they concluded that their sample still contained at least 1% of an absorbing impurity (acenaphthene ?).

It thus appeared possible that pure fluorene would be found not to have any absorption bands in the "diyl" region, a result which would be in agreement with the findings with dihydrophenanthrene. Attempts were therefore made to purify fluorene by recrystallisation from alcohol, but measurements made after five and after ten recrystallisations showed definite increases in the height of the bands between 375 and 300 mμ, indicating that the impurity was becoming more concentrated. The later samples were markedly fluorescent.

It was therefore decided to examine a specimen not obtained directly from coal-tar, but regenerated from a purified derivative. Through the courtesy of the Gesellschaft für Teerverwertung, Duisberg-Meiderich, a sample of fluorene was obtained from fluorenecarboxylic acid (prepared by the action of carbon dioxide on the sodium compound of fluorene; Weissgerber, *Ber.*, 1908, **41**, 2913); this had m. p. 116—117° and gave the spectrum reproduced in Fig. 5. No trace was observed of the bands between 375 and 300 mμ, though the specimen was photographed in concentrations up to 0·5%. The maximum observable at 251 mμ in some specimens had also entirely disappeared. It is considered that the absorption spectrum recorded in Fig. 5 is that of pure fluorene.

SUMMARY.

(1) The ultra-violet absorption spectra of the following reduced hydrocarbons related to the sterol nucleus have been measured : 9 : 10-dihydrophenanthrene, tetrahydrophenanthrene, two isomeric octahydrophenanthrenes, *cis-* and *trans*-hexahydrochrysenes, and 7 : 8-dihydrophenalyl-7-*spirocyclo*pentane.

(2) It has been shown that previous measurements of the absorption spectrum of fluorene have been made on impure materials, and the absorption of pure fluorene has now been measured.

(3) The data presented are consistent with the structures of these compounds. A relation is suggested between the type of spectrum and the position of the benzenoid nucleus in these compounds.

(4) The results obtained with fluorene and dihydrophenanthrene confirm Clar's theory concerning the relation between part of the spectrum and the reactive state of condensed polynuclear hydrocarbons.

117. *Preparation of* d-*Mannuronic Acid and its Derivatives.*

By R. G. AULT, W. N. HAWORTH, and E. L. HIRST.

THE occurrence of sugar units of the uronic acid type in many plant products and in the soluble specific polysaccharides having immunological importance has led us to seek methods for the preparation of these substances in reasonable yield in order that they may be available for synthetic work.

In the present paper the preparation of *d*-mannuronic acid from α-methylmannoside is described. We first prepared *α-methylmannoside* 2 : 3-*monoacetone* along with α-methyl-mannoside 2 : 3-4 : 6-diacetone, both of which are crystalline. The former of these serves admirably as a starting material, and alkaline permanganate oxidises the terminal group (6) to a carboxyl group, and the *potassium* salt of the resulting acid, α-methylmannuronide monoacetone, was isolated. Elimination of the acetone residue gave a crystalline potassium salt of α-methylmannuronide and also α-methylmannuronide, m. p. 108°, $[\alpha]_{5780}^{19°} + 65·6°$ in water, and finally *d*-mannuronolactone was isolated, m. p. 143—144°, $[\alpha]_D^{20°} + 95°$ in water. The optical rotation is slightly higher than has previously been recorded (compare Niemann and Link, *J. Biol. Chem.*, 1933, 100, 407).

Inasmuch as subsequent studies of natural products by the methylation procedure may result in the isolation of a methylated residue of mannuronic acid we have prepared and investigated the *methyl* ester of 2 : 3 : 4-α-methylmannuronide.

EXPERIMENTAL.

α-Methylmannoside 2 : 3-*Monoacetone.*—α-Methylmannoside (15 g.) was shaken for 24 hours with dry acetone (500 c.c.) containing 1% hydrochloric acid. The process was continued until all the solid had dissolved (10 days). The acetone extracts were neutralised (silver carbonate) immediately after decantation. They were finally united and evaporated in the presence of barium carbonate. The resulting syrup was extracted with boiling light petroleum (b. p. 40—60°), which removed α-methylmannoside diacetone together with condensation products of acetone. *α-Methylmannoside monoacetone* was left as a viscid syrup, b. p. 145°/0·02 mm., which soon crystallised and on recrystallisation from alcohol–light petroleum had m. p. 105°, $[\alpha]_D^{20°} + 28·3°$ in methyl alcohol (*c*, 4·3), $[\alpha]_D^{20°} + 24·3°$ in water (*c*, 4·0); yield, 6 g. The substance was readily soluble in all the usual solvents except light petroleum (Found : C, 51·1; H, 7·7; OMe, 13·3; Me₂CO, 24·5. C₁₀H₁₈O₆ requires C, 51·3; H, 7·7; OMe, 13·2; Me₂CO, 24·8%).

The pyranose structure of this substance was proved by its hydrolysis in the presence of *N*/100-hydrochloric acid at 15° to give quantitatively α-methylmannopyranoside, m. p. 195°, $[\alpha]_D + 79°$ in water (*c*, 1·0). The properties of α-methylmannoside 2 : 3-4 : 6-diacetone, m. p. 76°, will be described in a later paper.

Oxidation of α-*Methylmannoside* 2 : 3-*Monoacetone.*—This substance (6 g.), dissolved in water (100 c.c.), was oxidised by aqueous alkaline potassium permanganate (900 c.c. containing 8·1 g. of potassium permanganate and 3 g. of potassium hydroxide). After 24 hours at 15—20° the liquid was filtered, neutralised (carbon dioxide), and evaporated to dryness at 40°/12 mm. The resulting solid was extracted several times with alcohol, and the filtered extract concentrated to a viscid syrup. This was extracted with cold acetone and the acetone extract was evaporated to a syrup, which was dissolved in a little ethyl alcohol. On the addition of ether a viscid syrup was precipitated which, after purification by successive precipitations from alcohol, was obtained as a white amorphous hygroscopic powder. This was the *potassium* salt of α-methylmannur-onide monoacetone, $[\alpha]_D^{20°} - 4·5°$ in water (*c*, 3·9), (yield, 6·5 g.) (Found : OMe, 13·9; Me₂CO, 18·6; K, 13·7. C₁₀H₁₅O₇K requires OMe, 10·8; Me₂CO, 20·3; K, 13·6%).

α-Methyl d-*Mannuronide.*—The potassium salt of α-methylmannuronide (6·5 g.) was dissolved in water and 24·8 c.c. of *N*-hydrochloric acid were added (1 mol.). Further acid was added to make the mineral acid concentration *N*/50 and the solution was kept at 50° for 1 hour. During this time the observed rotation (1 dm. tube) changed from $\alpha_{5780}^{20°} + 0·27°$ to the constant value + 1·19°. The final solution was non-reducing. After neutralisation (silver carbonate) and concentration (diminished pressure) a syrup was obtained which was slightly contaminated with mineral matter. After solution in water, filtration, and evaporation of most of the solvent, followed by addition of ethyl alcohol at 70°, the crystalline *potassium* salt of α-methyl *d*-mannur-

onide was obtained as fine needles (4·55 g.) which contained alcohol of crystallisation. The salt decomposed without melting at about 230°. $[\alpha]_{5780}^{17°} + 48°$ in water (c, 1·5) (Found : OR, calc. as OMe, 16·9; K, 14·6. $C_7H_{11}O_7K,\frac{1}{4}C_2H_5\cdot OH$ requires OR, 17·3; K, 14·5%). An amorphous variety of this salt (free from combined alcohol) was obtained by precipitation of a concentrated aqueous solution with acetone (Found : OMe, 12·5. $C_7H_{11}O_7K$ requires OMe, 12·6%). On treatment with aqueous alcohol this was transformed into the above crystalline derivative. Both salts gave a strong positive Tollens–Neuberg reaction for uronic acid.

The above potassium α-methylmannuronide (1·8 g.) in water (2 c.c.) was treated at − 10° with the exact equivalent of perchloric acid, alcohol being added to complete the precipitation of the potassium perchlorate. The filtered solution was concentrated under diminished pressure at 25° to a syrup, which was dissolved in alcohol. After filtration and removal of the alcohol a syrup remained which was crystallised from alcohol–ether at − 10°, giving the *monohydrate* of α-methylmannuronide as rosettes of long needles, m. p. 108°, $[\alpha]_D^{19°} + 65·6°$ in water (c, 1·2). Yield, almost quantitative (Found : C, 37·4; H, 6·4; OMe, 14·5. $C_7H_{12}O_7,H_2O$ requires C, 37·2; H, 6·2; OMe, 13·7%). Aqueous solutions of the acid did not show mutarotation. The hydrated acid was readily soluble in water, moderately soluble in methyl alcohol, ethyl alcohol, and only slightly soluble in other solvents. The water of crystallisation was held firmly and was removed slowly and with difficulty by heating in a vacuum at 80—90°.

d-*Mannuronolactone.*—α-Methylmannuronide (0·8 g.) was boiled with 2·5% hydrochloric acid (25 c.c.) for 9 hours, the hydrolysis being followed polarimetrically ($[\alpha]_D^{20°} + 50°$ approx. Constant value after completion of hydrolysis). After neutralisation with silver carbonate, filtration, and removal of the dissolved silver by titration with hydrochloric acid, the solution was evaporated to a syrup (0·7 g.) under diminished pressure. Crystallisation of the d-mannuronolactone was brought about by very slow evaporation of an aqueous solution of the syrup containing a little ether. A similar method was used for recrystallisation. Broad plates, m. p. 143—144°. $[\alpha]_D^{20°} + 95°$ in water (c, 3·0). No mutarotation. The yield of recrystallised lactone was low (5—10%) (Found : C, 41·0; H, 4·7. Calc. for $C_6H_8O_6$: C, 40·9; H, 4·6%).

Methyl Ester of 2 : 3 : 4-*Trimethyl* α-*Methylmannuronide.*—Potassium α-methylmannuronide (3 g.) was methylated in the usual way with methyl sulphate (18 c.c.) and potassium hydroxide (20·5 g. in 30% aqueous solution). After the completion of reaction the solution was cooled to 20° and neutralised exactly by addition of dilute sulphuric acid. After evaporation to dryness (diminished pressure) the product was extracted from the solid residue by boiling absolute alcohol. The alcoholic extract was filtered, and concentrated to a syrup, which was dissolved in the minimum amount of water. After addition of sulphuric acid the liberated 2 : 3 : 4-trimethyl α-methylmannuronide was extracted by shaking with chloroform. This gave a syrup, which was dissolved in methyl iodide and boiled with silver oxide in the usual way, giving (after one repetition of the treatment with methyl iodide and silver oxide) the *methyl* ester of 2 : 3 : 4-trimethyl α-methylmannuronide as a colourless mobile syrup, b. p. 118°/0·02 mm., $n_D^{18°}$ 1·4523; $[\alpha]_{5780}^{20°} + 74°$ in methyl alcohol (c, 1·0); + 61·4° in chloroform (c, 1·0) (Found : C, 50·0; H, 7·5; OMe, 58·3; CO_2Me, 22·5. $C_{11}H_{20}O_7$ requires C, 50·0; H, 7·6; OMe, 58·7; CO_2Me, 22·4%). The ester was readily soluble in most organic solvents and moderately soluble in water (yield, 60%).

On hydrolysis with boiling N-sodium hydroxide the above ester gave the corresponding sodium salt, from which 2 : 3 : 4-trimethyl α-methylmannuronide was liberated by addition of the appropriate quantity of sulphuric acid. The product was removed from the aqueous solution by shaking with chloroform, and distillation yielded the pure substance as a viscid syrup, b. p. 156—158°/0·02 mm., $[\alpha]_{5780}^{21°} + 73°$ in methyl alcohol (c, 1·1) (yield, almost quantitative). 2 : 3 : 4-*Trimethyl* α-*methyl*-d-*mannuronide* was soluble in water and all the usual solvents (Found : C, 48·2; H, 7·1; OMe, 50·1. $C_{10}H_{18}O_7$ requires C, 48·0; H, 7·2; OMe, 49·6%). The amide, the phenylhydrazide, and various salts were prepared and examined, but none of these has yet crystallised.

118. *The Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents. Part III. The Effect of Unipolar Substituents on the Critical Energy and Probability Factors in the Interaction of Benzyl Bromide with Pyridine and α-Picoline in Various Solvents.*

By John W. Baker and W. S. Nathan.

Earlier results (Baker, J., 1934, 987; cf. J., 1933, 1128), derived from preliminary kinetic studies of the interaction of benzyl bromides with pyridine, indicated the necessity for a detailed kinetic analysis of this reaction, especially in relation to the effects of various factors upon its critical energy. Accurate data are now recorded for the energy of activation of the reaction between substituted benzyl bromides with pyridine and α-picoline in dry and in aqueous acetone and in aqueous alcohol, and the effects of both the base and the solvent on the various terms in the modified Arrhenius equation $k_p = PZ \cdot e^{-E/RT}$ are analysed. For reasons previously discussed (*loc. cit.*), the investigation is restricted, at present, to substituents of a unipolar $(\pm I)$ type.

In Part II (*loc. cit.*) it was shown that the velocity of interaction of benzyl halides and dry acetone (solvent reaction) was small (1—2%) in comparison with that of their reaction with pyridine. Improved methods of purification of materials have now reduced the velocity of such solvent reactions ($k_s{}^* = 7 \times 10^{-8}$ sec.$^{-1}$) to approximately 0·5% of that of the main reaction, and this can be ignored as being well within the probable experimental error (1—2%).

The essential bimolecular nature of the reaction, previously established for benzyl bromide (Part II), was first confirmed in the case of the *p*-nitro-derivative by variation in the concentration of both reactants. The data are summarised in Table I (time throughout is in seconds). A slight upward drift in the value of k_p is again observed in the presence

Table I.

Effect of concentration on the velocity of interaction of p-$NO_2 \cdot C_6H_4 \cdot CH_2Br$ (c_a) and pyridine (c_p), in dry acetone at 40°.

c_a.	c_p.	c_a/c_p.	$k_p \times 10^4$.	c_a.	c_p.	c_a/c_p.	$k_p \times 10^4$.
0·0125	0·0125	1	4·217	0·0250	0·0125	2·0	4·417
0·0050	0·0125	0·4	4·467	0·0250	0·0025	10·0	4·833

of a *large* excess of the bromide. This drift is probably explained by the superimposition of the small solvent reaction, which becomes relatively more important when the concentration of the pyridine is very small, and the rather larger experimental error involved in measurements at such dilution. Moreover, determination of the uncombined pyridine (Table II) by the method described on p. 525 shows clearly that throughout the reaction the free base disappears at the same rate as that at which the bromide ion is formed. The reaction is thus of the first order with respect to each reactant.

Table II.

Interaction of CH_2PhBr with pyridine, both 0·025M, in dry acetone at 30° (20-c.c. samples).

Time, mins.	0	10	1040	1400	2590
C.c. of $N/20$-NH_4SCN equiv. to unchanged CH_2PhBr	(10)	9·94	7·27	6·48	5·12
C.c. of $N/20$-H_2SO_4 equiv. to free C_5H_5N	(10)	9·94	7·26	6·42	5·19

In Part II, the catalytic influence of added salts was suggested, but more detailed investigations have revealed the existence of a definite equilibrium

$$ArBr + ArC_5H_5\overset{\oplus}{N}\}\overset{\ominus}{N}O_3 \rightleftharpoons ArO \cdot NO_2 + ArC_5H_5\overset{\oplus}{N}\}\overset{\ominus}{Br}$$
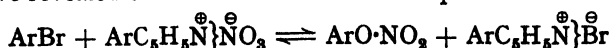
* As in Part II, k_s = the pseudo-unimolecular velocity coefficient for the solvent reaction, k_p = the *true* bimolecular velocity coefficient for the reaction with the cyclic base; c_a, c_p, and c_s are, respectively, the concentrations of aryl halide, cyclic base, and salt, in g.-mol. per litre.

which is established with a measurable velocity. The kinetics of this reversible reaction are under investigation, but meanwhile it must be noted that such interaction of the foreign anion with the benzyl bromide vitiates the use of the standard conditions of comparison $(c_a = c_p = c_s = 0.025$ g.-mol./l) previously employed. The quaternary bromide formed exerts a definite, although small, catalytic influence upon the reaction between benzyl bromide and pyridine in dry acetone. The data are in Table III.

TABLE III.

Effect of benzylpyridinium bromide (s) on the velocity of interaction of benzyl bromide with pyridine in dry acetone at 30° $(c_a = c_p = 0.025)$.

c_s	0	0.0129	0.0259
Bimol. $k \times 10^4$ (sec.$^{-1}$)	2.430	2.550	2.613
Mean deviation from mean $\times 10^4$	0.012	0.023	0.033

The slight upward drift observed in the bimolecular coefficient after about 40% reaction is explained by this effect superimposed upon the small solvent reaction which has been neglected. Such acceleration is negligible within the first 30—40% of the reaction. Hence the standard conditions employed throughout this paper are $c_a = c_p = 0.025M$, without added salt, velocity measurements being restricted to the first 20—30% of the reaction.

The data obtained under such standard conditions for the reaction between various benzyl bromides with pyridine or α-picoline in dry and aqueous 90% acetone and in 90% alcohol (both by wt.) at various temperatures are summarised in Table IV. The k_p values (in g.-mol./l./sec.) have been determined from the slope of the straight line obtained by plotting $x/(a-x)$ against time, and, in the case of 90% alcohol, are corrected for the solvent reaction as described in Part II.* Within the limits of experimental error, the plot of $\log_e k$ against $1/T_{abs}$ in all cases gives a straight line, from the slope of which the value of E has been determined. The values of Z are the theoretical collision values (at 30°) obtained from the relationship $5.71 \times 10^{25} . T^{\frac{1}{2}}[(M_1 + M_2)/M_1M_2]^{\frac{1}{2}}[(\sigma_1 + \sigma_2)/2]^2$ (Moelwyn-Hughes, *Chem. Reviews*, 1932, **10**, 241), molecular diameters being computed on the basis of parachor values (Nathan and Watson, J., 1933, 890). Substitution of α-picoline for pyridine makes a difference of only one unit in the third decimal place of $Z \times 10^{-11}$, so no appreciable error is introduced by using the same values throughout. The recorded mean values of P (the probability factor) are those derived from the modified Arrhenius equation $k_p = PZ . e^{-E/RT}$, whence the calculated values of k_p (col. 6) are derived.

Discussion.—Any discussion of the data summarised above falls naturally into two sections, *viz.*, (A) conclusions which seem to be fairly definitely established by the experimental results, and (B) tentative suggestions which may partly explain some of the more complicated phenomena and also indicate further lines of investigation with a view to testing their validity.

(A) It has already been suggested (Part II) that it is not possible to separate the energy requirements of the two processes (of opposite polar requirements) involved in the formation of the quaternary bromide, *viz.*, (1) the anionisation of the bromine, and (2) the electrostriction and co-ordination of the base to the carbon. This conclusion would seem to be definitely established by the observation that the activation energies for the reaction of all three benzyl bromides with pyridine are almost identical with the corresponding values in the interaction with α-picoline, in spite of the fact that the basic strength of the latter $(K_b = 3 \times 10^{-8})$ is ten times as great as that of the former $(K_b = 2.3 \times 10^{-9})$, a factor which must greatly facilitate process (2). Moreover, in each series, the activation energies of the p-methyl- and p-nitro-derivatives differ but slightly from that of the unsubstituted parent. Such observations, coupled with the bimolecular character of the reaction, clearly indicate that, in non-ionising solvents, the reaction mechanism is

* The solvent reaction in 90% acetone is of the same order $(k_s = 7 \times 10^{-6}$ sec.$^{-1}$ with benzyl bromide) as that in dry acetone, and is still within the limits of the experimental error.

TABLE IV.

Kinetic data for the interaction of p-$C_6H_4R\cdot CH_2Br$ with pyridine (Py.) and α-picoline (Pic.) in various solvents ($c_a = c_p = 0.025M$).

No.	Base.	R.	Temp.*	$k_p \times 10^4$. Found.	$k_p \times 10^4$. Calc.†	E, cals.	P × 10⁴.	Z × 10⁻¹¹ (at 30°).
I. *In dry acetone.*								
1	Py.	H	0°	0·248	0·247			
2	,,	H	20	1·223	1·236			
3	,,	H	30	2·450	2·496	12,460	0·870	2·776
4	,,	H	40	4·817	4·818			
5	,,	Me	0	0·420	0·426			
6	,,	Me	20	2·020	1·980			
7	,,	Me	30	3·900	3·887	11,900	0·515	2·866
8	,,	Me	40	7·150	7·250			
9	,,	NO₂	0	0·231	0·231			
10	,,	NO₂	20	1·122	1·132			
11	,,	NO₂	30	2·267	2·269	12,310	0·607	2·816
12	,,	NO₂	40	4·333	4·344			
13	Pic.	H	20	0·183	0·181			
14	,,	H	30	0·367	0·365	12,480	0·132	2·776
15	,,	H	40	0·705	0·701			
16	,,	Me	20	0·328	0·326			
17	,,	Me	30	0·647	0·648	12,190	0·139	2·866
18	,,	Me	40	1·240	1·232			
19	,,	NO₂	20	0·127	0·126			
20	,,	NO₂	30	0·248	0·249	12,100	0·0470	2·816
21	,,	NO₂	40	0·475	0·472			
II. *In aqueous 90% acetone.*								
22	Py.	H	20	2·342	2·345	13,710	13·97	2·776
23	,,	H	40	10·470	10·468			
24	,,	Me	20	4·200	4·200	13,680	23·17	2·866
25	,,	Me	40	18·700	18·622			
26	,,	NO₂	20	1·580	1·581	13,840	11·70	2·816
27	,,	NO₂	40	7·167	7·163			
III. *In aqueous 90% alcohol.*								
28	Py.	H	20	1·297	1·290	15,310	120·81	2·776
29	,,	H	30	3·075	3·095			
30	,,	Me	20	2·840	2·830	16,000	836·74	2·866
31	,,	Me	30	7·000	7·026			
32	,,	NO₂	20	0·422	0·419	15,810	91·377	2·816
33	,,	NO₂	30	1·029	1·036			

* Temperatures recorded as 0°, 20°, 30°, 40° are actually − 0·5°, 20·0°, 29·95°, and 39·9°, respectively, as determined by a calibrated N.P.L. standard thermometer.

† The relative values of k_p are probably accurate to 1—2%, although systematic errors essential to the technique probably make the *absolute* values subject to an error of 3—4%. The probable error in E values determined from velocity data at three or four temperatures (Section I) is of the order of 100 cals., but in those determined at only two temperatures (Sections II and III), a somewhat larger error may be anticipated, especially in Section III, where the correction for the solvent reaction is relatively large.

essentially one of simultaneous addition and dissociation of the type proposed by London (*Z. Elektrochem.*, 1929, **35**, 552) on quantum-mechanical grounds, and recently discussed by Hughes and Ingold (this vol., p. 244; mechanism S_N2) in their generalised theory of reaction at a saturated carbon atom : $C_5H_5N \overset{\frown}{} Ar \overset{\frown}{} Br \longrightarrow \overset{\oplus}{\cdot}C_5H_5NAr + \overset{\ominus}{Br}$. A precisely similar conclusion has been reached by Hammett and Pfluger (*J. Amer. Chem. Soc.*, 1933, **55**, 4079) in the case of the comparable reaction between trimethylamine and alkyl acetates.

Another interesting aspect of the results is revealed by the velocity ratios for the substituted and the unsubstituted benzyl bromides given in Table V, in which the ratios of the probability factors are also shown.

It has already been established (Part II) that the effect of unipolar substituents on velocity varies enormously from reaction to reaction, even although *all* such reactions

M M

TABLE V.

The effect of the substituent R on the velocity of interaction of p-$C_6H_4R\cdot CH_2Br$ with pyridine and α-picoline in various solvents.

R.	Temp.	Dry $COMe_2$.		90% $COMe_2$		90% EtOH.	
		k_R/k_H.	P_R/P_H.	k_R/k_H.	P_R/P_H.	k_R/k_H.	P_R/P_H.
Pyridine.							
Me	0°	1·69 ⎫		— ⎫		— ⎫	
,,	20	1·66 ⎟		1·79 ⎟		2·19 ⎟	
,,	30	1·59 ⎬ 0·59		— ⎬ 1·65		2·28 ⎬ 6·9	
,,	40	1·48 ⎭		1·79 ⎭		— ⎭	
NO_2	0	0·93 ⎫		— ⎫		— ⎫	
,,	20	0·917 ⎟		0·675 ⎟		0·325 ⎟	
,,	30	0·925 ⎬ 0·70		— ⎬ 0·84		0·334 ⎬ 0·76	
,,	40	0·900 ⎭		0·717 ⎭		— ⎭	
α-Picoline in dry acetone.							
R=Me	$t=$ 0	1·84 ⎫		R=NO_2 $t=$ 0		0·696 ⎫	
,,	20	1·76 ⎬ 1·05		,, 20		0·663 ⎬ 0·35	
,,	30	1·76 ⎭		,, 30		0·674 ⎭	

involve attack by nucleophilic reagents and anionisation of the halogen in the formation of the ultimate product. The results in Table V now clearly indicate that the effect of such substituent groups upon the velocity of one particular reaction is largely dependent upon the nature of the medium,* and, to a smaller extent, upon that of the base. This is especially noticeable in the case of a p-nitro-substituent, a group which has always been considered to exert a strong retarding influence upon reactions which require electron accession to the side chain. Such retarding influence is clearly marked in 90% alcohol but is almost non-existent in dry acetone, the velocity of the p-nitro-compound in this medium being 90—95% of that of the unsubstituted parent. In the face of such results, it seems difficult any longer to assume, at least in the example of quaternary-salt formation in non-ionising media under consideration, that the general inductive polar effect of substituents is concerned mainly with the degree of polarisation or with the polarisability of the carbon–halogen bond. This differentiation in the effects of unipolar substituents upon velocity leads us naturally into a more detailed consideration of the effect of solvent upon the various factors in the reaction.

(B) Examination of the data in Table IV leads to the following clearly defined experimental conclusions, quite independently of any theoretical interpretation. Consideration being restricted first to the reaction with pyridine, it is apparent that in the solvent series dry acetone (Nos. 1—12), aqueous acetone (Nos. 22—27), and aqueous alcohol (Nos. 28—33), *i.e.*, in a series representing increasing ionising power, the continual increase in velocity is accompanied by a parallel *increase* (1) in the energy of activation (12,000 to 16,000 cals.), and (2) in the magnitude of the retarding or accelerating effect of the p-substituent group, *i.e.*, in the relative separation of the velocities of the unsubstituted and the substituted benzyl bromides. In any one solvent, the activation energies of the three benzyl bromides are almost identical, the differentiation in their velocities being accounted for almost entirely by the different values of the probability factor. These P factors, which are small and essentially the same for all three derivatives in dry acetone, become increasingly larger and also increasingly divergent in aqueous acetone and in aqueous alcohol (cf. Table V). In this connexion, it is of interest that Hughes (this vol., p. 255) found that the E value for the unimolecular ionisation of chlorine from carbon, in the case of *tert.*-butyl chloride in aqueous 80% acetone, is of much higher order, *viz.*, 22,600 cals. This value is closely similar to those which we have observed (Table VI) for the (probably pseudo-unimolecular) reaction between the aryl halides and aqueous 90% alcohol (the solvent reaction). Such data suggest that, in aqueous solvents, the reaction mechanism of quaternary-salt formation may approach

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* A similar result was established by McCombie, Scarborough, and Smith (J., 1927, 802) for the reaction between o-, m-, and p-nitrobenzyl chlorides with trimethylamine.

the type (whatever that may be *) involved in the hydrolysis reactions. The present results supply no evidence for the existence of a superimposed unimolecular reaction, $Ar—Br \longrightarrow \overset{\oplus}{Ar} + \overset{\ominus}{Br}$; $\overset{\oplus}{Ar} + C_5H_5N \longrightarrow C_5H_5\overset{\oplus}{N}Ar$, in dry acetone, but it has previously been suggested (Baker, J., 1932, 2631) that, in aqueous 90% alcohol, *p*-methoxy-benzyl bromide *does* react by this mechanism, the initial ionisation in this case being rapid.

TABLE VI.

Action of aqueous 90% EtOH (by wt.) on *p*-C$_6$H$_4$R·CH$_2$Br.

R.	Temp.	Unimol. $k_a \times 10^6$, sec.$^{-1}$	E (Arrhenius), cals.
H	20°	0·817	
H	30	3·17	23,910
Me	20	3·53	
Me	30	12·0	23,870
NO$_2$	20	0·125	
NO$_2$	30	0·350	22,870

The conversion of a neutral pyridine molecule into the positively charged pyridinium cation, *e.g.*, in its reaction with an acid, is an exothermic reaction, and it is tentatively suggested that the similar conversion of pyridine into the benzylpyridinium cation, once the (probably low) energy barrier is surmounted, liberates energy which may be utilised in the concomitant ionisation of the bromine atom, thus accounting for the much lower energy of activation observed in the bimolecular reaction.

It is considered almost certain that in dry acetone the attacking reagent is a pyridine *molecule*, but in aqueous media the formation of pyridinium complexes, of varying degrees of electrostriction up to the limiting type $C_5H_5\overset{\oplus}{N} \longrightarrow \overset{\ominus}{H}·OH$, might be anticipated. The interaction of such complexes with the aryl halides to form the quaternary salt must involve the rupture of the co-ordinate link between the nitrogen atom and the water molecule :

$$HO·H \leftarrow NC_5H_5 \quad Ar—Br \longrightarrow Ar\overset{\oplus}{N}C_5H_5\}\overset{\ominus}{Br} + H_2O$$
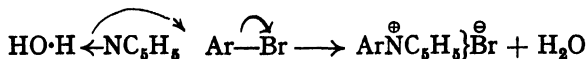
and the additional energy requirements of this stage might account for the larger energy of activation observed in aqueous acetone and alcohol. On this view, the higher energy of activation required in the hydrolysis of the aryl bromide in aqueous alcohol (Table VI) could be regarded as arising from the necessary rupture of a normal covalent link between oxygen and hydrogen :

$$H—OH \quad Ar—Br \longrightarrow ArOH + HBr.$$

The relatively greater effects of *p*-methyl (accelerating) and *p*-nitro (retarding) substituents in aqueous media could then be correlated with their effects in facilitating and preventing, respectively, the appropriate orientation of the attacking charged complex to the α-carbon. It is significant that, as already noted, the greater differentiation between the velocities of the *p*-methyl, *p*-hydrogen, and *p*-nitro-derivatives in aqueous media (Table IV, Sections II and III) depends mainly on the P and not on the E term in the modified Arrhenius equation. In reactions where the approach of a charged ion and not a neutral molecule is involved, the presence of the charge upon the attacking entity may, we think, introduce further complications, particularly with regard to the orientation and approximation of the attacking reagent to the seat of attack. Thus in attack by a negatively charged ion upon a saturated carbon atom, the ion must penetrate the surrounding electronic field of the atom, and this may well be an important factor in determining the critical increment of such reactions. It is anticipated that the critical-energy

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* The possibility of the formation of an intermediate complex, which may then decompose unimolecularly, $ArBr + C_5H_5N \underset{k_2}{\overset{k_1}{\rightleftharpoons}} complex \overset{k_3}{\longrightarrow} product$, must be kept in mind. The reaction kinetics in such a case would then depend upon the relative magnitudes of k_1, k_2, and k_3.

increments and velocities of the forward and the reverse reaction in the salt equilibrium referred to on p. 519, which is essentially an attack by a negative ion, $ArBr + \overset{\ominus}{N}O_3 \rightleftharpoons$ $ArO \cdot NO_2 + \overset{\ominus}{Br}$, will throw light on this aspect of the problem.

In conclusion, two other points must be briefly discussed. The first is the much slower reaction observed with the stronger base α-picoline (Nos. 13—21) than with the weaker base pyridine (Nos. 1—12) under otherwise identical conditions. It will be noticed (Table IV) that the E terms with both bases are practically identical, the velocity differentiation being accounted for entirely by the smaller value of the probability factor in the former case. We suggest that this is due largely to the steric effect of the α-methyl group, possibly accentuated by an orientation effect due to the more pronounced polar character of the picoline molecule.

The second point is the rather lower value for E observed in the reaction between *p*-methylbenzyl bromide and pyridine. The difference (500—600 cals.) is larger than the estimated experimental error in this series, and suggests the existence of a real, but small, facilitating effect of the *p*-methyl group. Further discussion of this point would be premature until the results of work now in hand are available, particularly that part of it dealing with the effects of an extended series of unipolar substituents in both the meta- and the para-position.

EXPERIMENTAL.

Purification of Materials.—*Acetone.* Since large volumes of pure acetone were required, the feasibility of employing A. R. acetone (B.D.H.) was explored, but it was found that, even after drying with calcium chloride and careful fractionation through a column, the sample still showed considerable reactivity with benzyl bromide. Such reactivity, moreover, was not removed by refluxing a solution of benzyl bromide and pyridine (both 0·025M) in the acetone for 5 days, to complete quaternary-salt formation, and recovering the solvent by careful fractionation. The only satisfactory material is that regenerated from the sodium iodide compound (supplied by B.D.H.). This was dried for several days over sodium sulphate, fractionated through a column, and the process repeated on the constant-boiling fraction. The sample thus obtained, b.p. 56·2°, was almost free from activity towards pure benzyl bromide (Found : $k_{unimol.} = 0·71 \times 10^{-7}$ sec.$^{-1}$ in 0·025M-solution at 30°). The " heads " and " tails " from the fractionation were left in contact with a little solid potassium permanganate and sodium sulphate for 7 days, and again treated as above, a further quantity of suitable acetone being thus obtained. The aqueous acetone was prepared from this sample and distilled water by direct weighing. The aqueous alcohol was the sample used in Part II.

Benzyl bromides. Benzyl bromide was repeatedly fractionated under reduced pressure. The constant-boiling fraction was then gently refluxed, in the distillation apparatus, with a few drops of pure pyridine; the resulting hygroscopic quaternary salt removed any remaining traces of water. Refractionation gave a sample, b. p. 82°/11 mm., which was again distilled in a vacuum immediately prior to each velocity determination. The refractive index (not recorded in the literature) was $n_D^{22°}$ 1·5742. The *p*-methylbenzyl bromide was first purified by repeated crystallisation from ligroin (b. p. 40—60°), and the sample, m. p. 36·2°, was then distilled first with pyridine and finally alone, as in the case of benzyl bromide. *p*-Nitrobenzyl bromide was purified by repeated crystallisation, first from 95% alcohol and then from ligroin (b. p. 40—60°); m. p. 98·9°.

Pyridine. A " pure " commercial specimen (Monsanto) was dried over fused potassium hydroxide and repeatedly fractionated through a long pear-head column in an all-glass apparatus. The middle fraction was refluxed with a few c.c. of pure benzyl bromide, and again fractionated, only the middle fraction of constant b. p. 116·5° being employed.

α-Picoline. This was repeatedly fractionated, first under atmospheric pressure through a long column, and then repeatedly under reduced pressure until all low-(pyridine) and high-boiling fractions were eliminated. It was then treated with benzyl bromide, and the purification completed as for pyridine; b. p. 50·5—50·7°/38 mm.

Velocity Determinations.—The technique was essentially that previously used (*loc. cit.*) except that there was a tendency for a small amount of benzyl and *p*-methylbenzyl bromides to remain in the initial aqueous–acetone layer. To avoid this, the following technique was finally adopted. The reaction sample (20 c.c.) was run into about 80 c.c. each of water and ether, and the quaternary salt washed out by repeated extractions with 10—20 c.c. portions

of water. To the combined aqueous liquors, about 90% of the estimated volume of $N/20$-ammonium thiocyanate solution was added from a N.P.L. standard 10 c.c. burette, a few c.c. of pure nitric acid added, followed by 10 c.c. of $N/20$-silver nitrate (from a standard pipette). After addition of the ferric indicator, titration of the excess of silver nitrate was rapidly completed with the standard thiocyanate solution. In this manner, any minute trace of the aryl halide which might still have passed into the aqueous layer was only in contact with a very small concentration of silver nitrate for a short time, so that interaction between the two substances was negligible.

All samples were taken out at the temperature of the thermostat, pipettes being kept in suitable containers in the thermostat itself.

Since it was found unnecessary to stir the homogeneous reaction mixture, the velocity determinations were carried out in long-necked, stoppered, glass flasks instead of the more complicated apparatus previously employed.

Temperature control, by electrically operated thermo-regulators, was accurate to $\pm 0.02°$, as recorded on Beckmann thermometers, actual temperatures being determined by a N.P.L. standard thermometer. Measurements at $-0.50°$ were conducted in a rapidly stirred mixture

FIG. 1.
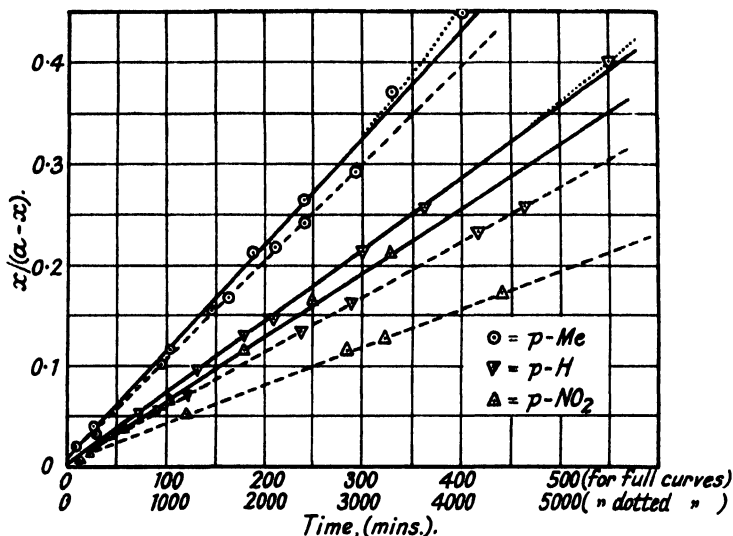
Full curves ——— $= C_6H_4R\cdot CH_2Br + pyridine\ in\ dry\ acetone\ at\ 40°.$
Dotted curves - - - $= C_6H_4R\cdot CH_2Br + a\text{-}picoline\ in\ dry\ acetone\ at\ 30°.$

of crushed ice and water in a bath suitably insulated in a packed wooden box. The Beckmann thermometer was, in this case, calibrated against the N.P.L. standard thermometer at 0° in a bath of melting ice prepared from pure distilled water.

Determination of Pyridine and a-Picoline.—In order to follow the reaction by observations of the rate of removal of the base, an empirical method for the rapid determination of very small concentrations of pyridine and a-picoline was developed. The reaction sample (20 c.c.) was pipetted into 5 c.c. of water and 30 c.c. of ether (to remove all the aryl bromide from the aqueous layer), and the base extracted with a known volume of $N/20$-sulphuric acid under standard conditions. The excess of acid in the aqueous layer was titrated with $N/20$-sodium carbonate and bromophenol-blue. The end point was taken at an intermediate green shade, which was matched against an artificial colour standard (an aqueous solution containing 0.075 g. of potassium dichromate and 1.5 g. of chrome alum per l.). The accuracy of the method (approx. 1%) was checked with known amounts of the two bases over the whole concentration range required.

	Pyridine, mg.					a-Picoline, mg.		
Taken	7·87	15·73	23·60	31·47	39·47	18·61	32·57	46·53
Found	8·10	15·68	23·55	31·32	39·14	18·46	32·42	46·45

Determination of the Velocity Coefficients.—The bimolecular velocity coefficient was derived from the value of $x/(a - x)t$, obtained from the slope of the best straight line of the $x/(a - x)-t$ graph. In all cases, deviation of individual values from the line was very slight (see Figs. 1

FIG. 2.
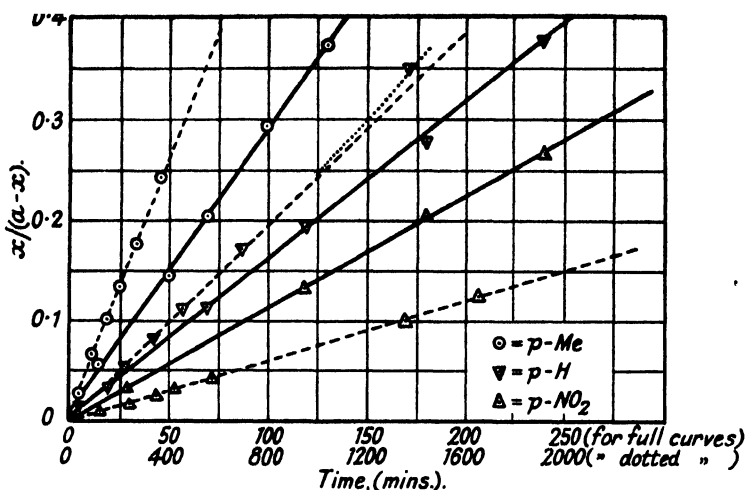
Full curves ——————— = $C_6H_4R\cdot CH_2Br$ + *pyridine in aqueous 90% acetone at 40°.*
Dotted curves – – – – = $C_6H_4R\cdot CH_2Br$ + *pyridine in aqueous 90% alcohol at 20°.*

and 2) but it may be noted that at $t = 0$ the curve sometimes indicated a value of $x/(a - x)$ corresponding to about 0·2—0·4% of bromide ion. This slight deviation from the origin is almost within the range of experimental error, but the possibility of the presence of a very

FIG. 3.
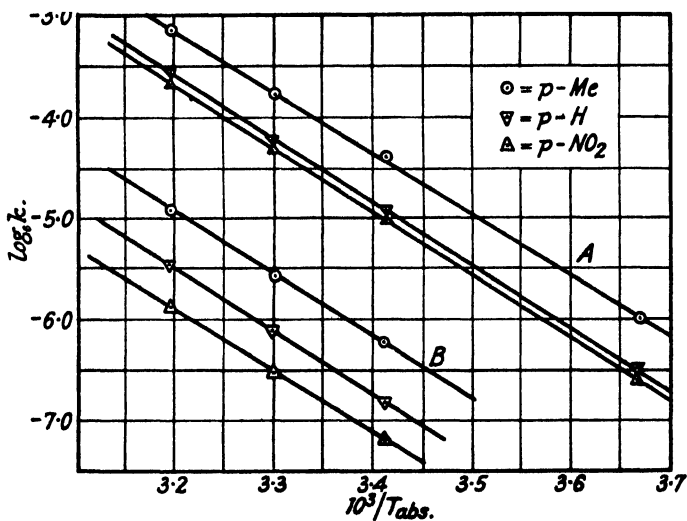
A = *Reaction with pyridine in dry acetone.*
B = *Reaction with α-picoline in dry acetone.*

small initial concentration of bromide ion arising from an equilibrium $ArBr \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \overset{\oplus}{Ar} + \overset{\ominus}{Br}$, in which k_2 (and, also, k_p) is very much greater than k_1, must not be overlooked. The degree of accuracy claimed for the results is substantiated by the reproduction of one typical set of curves in each series of velocity measurements, in Figs. 1 and 2. The plot of $\log_e k_p$ against

$1/T_{abs.}$ for experiments Nos. 1—12 (pyridine) and 13—21 (α-picoline) is given in Fig. 3. These curves clearly indicate the various experimental results discussed in this communication, especially the increasing differentiation between the velocities of the substituted and unsubstituted derivatives under the different experimental conditions.

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119. *Studies in Electro-endosmosis. Part VI. The " Bubble-tube" Method of Measurement.*

By FRED FAIRBROTHER and ALFRED E. STUBBS.

THE principle of this method of measurement of electro-endosmosis, introduced by Briggs, Bennett, and Pierson (*J. Physical Chem.*, 1918, **22**, 256) and used subsequently by other workers, is illustrated in Fig. 1. The true electro-endosmotic speed, V_t, through the capillary or porous diaphragm, D, is measured by the apparent velocity of flow, V_a, of the liquid through the single capillary or narrow tube, AA, as indicated by the linear speed, U_a, of the bubble of air, B, which is contained in the capillary.

FIG. 1.

In using a bubble-flowmeter in this way, it is assumed in the first place that the hydrodynamic resistance of the flow-meter capillary and its associated connecting tubes is negligible compared with that of the electro-endosmosis diaphragm. If this is not so, the pressure difference between the ends of the diaphragm, which is necessarily present for any flow to take place through the capillary, will cause a " back-flow " through the diaphragm itself, and the flow observed by the flowmeter will represent only part of the total electro-endosmotic flow. This condition, to a close approximation, can be achieved in practice by careful attention to the design of the apparatus.

There are also other assumptions involved which are less obvious. It must be assumed that the liquid does not flow round the bubble in the direction of motion. It was found in the present work that the minimum length of bubble necessary to avoid this source of error was $1\frac{1}{4}$ times the diameter of the tube; with bubbles of length equal to the diameter of the tube, the effect can readily be observed, and with shorter bubbles, especially if the speed is slow and the bubble-tube slightly contaminated, the effect may be so pronounced as to leave the bubble stationary.

It is also assumed implicitly that the layer of liquid wetting the walls of the bubble-tube is of negligible thickness, *i.e.*, that the bubble moves along as a closely fitting piston. The bubble, however, is bounded not only by a liquid meniscus at each end, but also by the film of liquid on the walls of the tube. When the bubble is in motion, this film, which has been left behind by the liquid moving in front of the bubble, becomes part of the liquid behind the rear meniscus, as the bubble passes along. The effective cross-sectional area of the tube is therefore diminished by this layer of liquid. Hence, if the *volume* flow of the liquid per second is calculated from the *linear* velocity of the bubble and the total cross-sectional area of the tube, the value obtained will be too high. The discrepancy from the true value would be expected to depend upon the rate of flow and on other factors, such as the surface tension and viscosity of the liquid, which affect the rate of drainage from the wetted surface. When only dilute aqueous solutions are employed, together with slow movements of the bubble, this effect, as will be shown, does not introduce errors
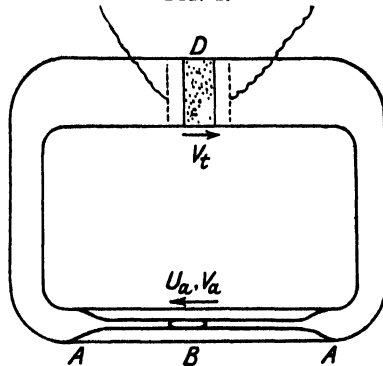
greater than a few units %. At higher speeds, on the other hand, or when organic liquids of widely differing physical properties are used, the errors introduced by this " wetting " or " drainage " effect may be large.

We have therefore examined experimentally the relationship between the true velocity of a liquid in a capillary tube and that indicated by the linear velocity of an entrained air bubble.

EXPERIMENTAL.

The experimental method consisted briefly in allowing the liquid under examination to flow at a constant rate through a long capillary tube which contained an air bubble whose velocity between two marks near the beginning and the end of the tube was observed by means of a stop-watch. The apparent velocity V_a of the liquid was calculated from the time of flow and the volume of the tube between the marks. A small correction was applied to the " volume " of the capillary tube when the bubble overshot the finishing mark, for it was not always easy to stop it exactly on the mark except at slow speeds. The liquid emerging from the capillary was caught in a small tared flask which was then stoppered. Capillary tubes of about 1 m. in length and 2·25 mm. in diameter were used. This bore was almost the same as that of the capillary tube used in the electro-endosmosis apparatus to be described in another paper. The present results could therefore be used to correct the apparent electro-endosmotic velocities obtained in this apparatus. The test of the expression given below with tubes of much greater or much smaller diameter is very difficult. With wider tubes the effect of gravity becomes noticeable, and the meniscuses are no longer symmetrical about the axis, whilst with narrower tubes the experimental error, caused largely by evaporation of the liquid during manipulation, becomes almost as large as the effect to be observed. It is reasonable to suppose, however, that the same expression holds for tubes of different diameters which are sufficiently small for the effect of gravity to be negligible in comparison to that of surface tension.

Experiments were carried out with a straight tube at room temperature (15—16°) and with loosely coiled tubes immersed in a thermostat at 20° : the results obtained in each case were very similar. A number of experiments carried out by Mr. H. P. Dakin with similar tubes and several aliphatic alcohols also confirm our results.

It was first established that, providing the bubble length was greater than about 1½ times the diameter of the tube, the difference between the apparent velocity of the liquid at a given rate of flow, as indicated by the bubble, and the true velocity was, within the experimental error, independent of the length of the bubble.

This difference between the velocities depends very greatly, however, on the rate at which the liquid and the bubble move through the capillary. The following table, which relates to the flow of water through a tube of 2·26 mm. diameter containing a bubble 1·5 cm. in length, illustrates this point. The last col. gives 100 W, the percentage error in the speed as estimated

U_a (cm./sec.).	V_a (c.c./sec.).	V_t (c.c./sec.).	$\frac{100(V_a - V_t)}{V_a}$.	U_a (cm./sec.).	V_a (c.c./sec.).	V_t (c.c./sec.).	$\frac{100(V_a - V_t)}{V_a}$.
0·79	0·0315	0·0312	1·1	8·5	0·3379	0·3253	3·7
1·4	0·0557	0·0548	1·5	9·1	0·3639	0·3496	3·9
3·1	0·1245	0·1216	2·3	12	0·4731	0·4531	4·2
3·6	0·1433	0·1397	2·5	16	0·631	0·598	5·1
4·4	0·1752	0·1704	2·7	22	0·860	0·810	5·9
4·7	0·1892	0·1836	3·0	30	1·182	1·097	7·1
5·9	0·2365	0·2289	3·2				

from the movement of the bubble. It will be observed that this " wetting " or " drainage " effect may give rise to errors of several units % in the estimated speeds of electro-endosmosis.

The difference between the true and the apparent speed is dependent upon the thickness, d, of the film of liquid adhering to the wall of the capillary. A simple calculation shows that if D is the internal diameter of the tube,

$$W = (V_a - V_t)/V_a = 4(D - d)d/D^2$$

or, if d is small compared with D,

$$W = (V_a - V_t)/V_a = 4d/D.$$

Experiments carried out with various liquids showed that in each case, with a given capillary and liquid, W was proportional to the square root of the linear velocity of the bubble. This is illustrated for four liquids in Fig. 2, in which is also given the calculated thickness d (in μ) of the layer of liquid on the walls of the tube.

The effect here observed is somewhat similar to that discussed by the Research Staff of the General Electric Company, London (*Phil. Mag.*, 1922, **44**, 1002), who examined, theoretically and practically, the problem of the thickness of the liquid layer covering a solid body drawn out of a liquid, as in many industrial processes for the coating of solid surfaces. They found that, if the solid is a flat slab of infinite width, drawn vertically with velocity V through the surface

FIG. 2.
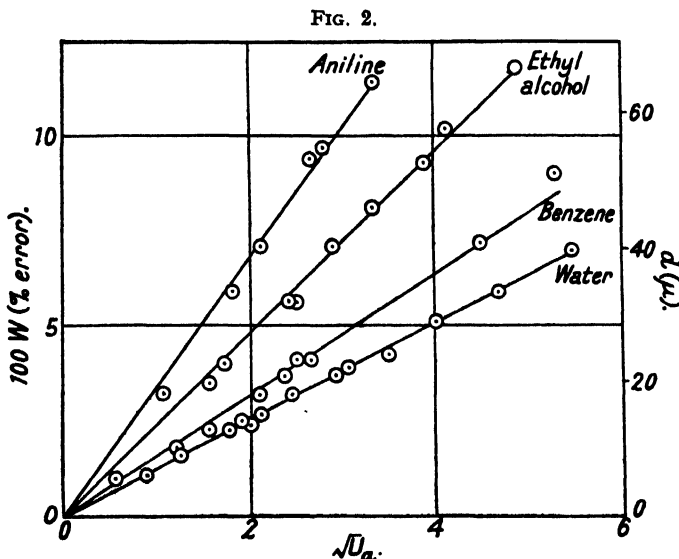
of a liquid of viscosity η and density ρ, the thickness t of the adherent film is approximately $t = \sqrt{2V\eta/g\rho}$. If the solid has a curved surface, the thickness of the adhering layer is also a function of the surface tension of the liquid, which, in the case of fine wires, becomes dominant.

In the case now under consideration, that of a horizontal capillary, the effect of gravity is negligible, and the chief factors concerned are the viscosity and surface tension of the liquid. It can be seen by qualitative inspection that these must act in opposite directions : the surface tension pulls the lagging film of liquid into the leading meniscus at a speed determined by the viscosity.

If we write $W = k\sqrt{U_a}$ and plot log k against log η/σ, where η and σ are respectively the viscosity and the surface tension of the liquid in question, both measured in C.G.S. units, we obtain a very close approximation to a straight line (Fig. 3) with a slope of $1/2$, which on

FIG. 3.

production passes through, or very close to, the origin. Hence it follows that we have to a first approximation the very simple empirical relation $W = 4d/D = \sqrt{U_a\eta/\sigma}$, which is also dimensionally correct.

The above results show that this effect is not by any means to be neglected in the measurement of electro-endosmosis by the bubble-tube method, except perhaps in the case of aqueous solutions over a small range of bubble speeds. Allowance may be made in any particular instance by carrying out a series of experiments as described here, or by use of the empirical relation given above. The effect is probably responsible for part, at least, of the non-linear relation between applied *E.M.F.* and electro-endosmosis observed by different workers.

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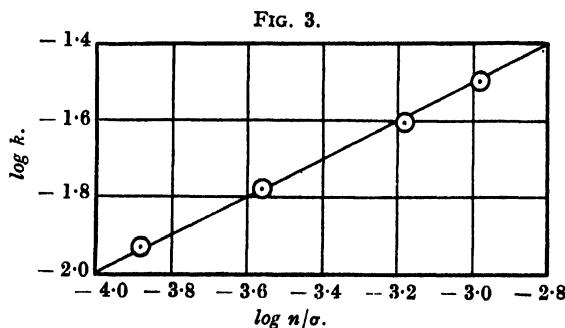
120. *The Tetrazotisation of Aryl Diamines with Special Reference to o-Phenylenediamine.*

By HERBERT H. HODGSON and JOHN WALKER.

SCHOUTISSEN (*J. Amer. Chem. Soc.*, 1933, **55**, 4531) has described a method of diazotisation (or tetrazotisation) in which a solution of the amine (or diamine) in concentrated sulphuric acid is mixed with nitrosylsulphuric acid (sodium nitrite dissolved in concentrated sulphuric acid) and diazotisation is effected by subsequent dilution with phosphoric acid. He thus succeeded in tetrazotising *p*-phenylenediamine and obtained from it a 70% yield of *p*-dichlorobenzene by the Sandmeyer process, but he practically failed in the case of *o*-phenylenediamine.

Prior to the publication of Schoutissen's paper, we had applied our method for the diazotisation of nitroamines (J., 1933, 1620) to aryldiamines and found it to be uniformly successful; in particular, *o*-phenylenediamine was tetrazotised without aziminobenzene formation and *o*-dichlorobenzene was obtained from it in 70% yield. Since nitrous acid is present always in excess, the occurrence of secondary reactions is reduced to a minimum or prevented altogether.

Solutions of *m*-tolylenediamine (24·4 g.) and of *o*-, *m*-, and *p*-phenylenediamine (21·6 g.), each in glacial acetic acid (150 c.c.), were added gradually, below 30°, to well-stirred solutions of nitrosylsulphuric acid (prepared by dissolution of sodium nitrite, 32 g., in concentrated sulphuric acid, 320 c.c., at 70°). Test portions poured into excess of water gave no indication of the formation of Bismarck brown from the *m*-diamines or of aziminobenzene from *o*-phenylenediamine. The tetrazo-solutions were poured gradually into solutions of cuprous chloride (40 g.) in concentrated hydrochloric acid (300 c.c.) below 40°, and when the evolution of nitrogen ceased, the mixtures were diluted each with an equal volume of water and steam-distilled. The volatile oils were washed with aqueous caustic alkali and with water, dried, and distilled. The diamines in the order mentioned above gave 24·2 g. of 2 : 4-dichlorotoluene (Found : Cl, 44·0. Calc. : Cl, 44·1%), 20·6 g. of *o*-dichlorobenzene (Found : Cl, 48·1. Calc. : Cl, 48·3%), 20·7 g. of *m*-dichlorobenzene (Found : Cl, 48·2%), and 20·5 g. (crystallised from alcohol) of *p*-dichlorobenzene, m. p. 53° (Found : Cl, 48·1%).

The authors thank Imperial Chemical Industries Ltd. (Dyestuffs Group) for various gifts.

121. *Organic Compounds of Sulphur. Part XXV.* The Interaction between Organic Azides and Aromatic Thio-ketones and a New Method of converting the Azido-group into the Amino-group.*

By ALEXANDER SCHÖNBERG and W. URBAN.

ALTHOUGH organic azides (*e.g.*, phenyl-, benzyl-, and benzenesulphon-azide) are very reactive compounds, they have not been made to react with the carbonyl group of ketones. We have found, for example, that benzophenone reacts neither in the cold nor on prolonged heating with phenylazide. In this as in other cases (cf. Schönberg, " Sammlung chemischer und technisch-chemischer Vorträge," No. 19, Enke, Stuttgart), however, the corresponding thioketones possess superior reactivity and it has been possible to bring about interaction of azides and thioketones with formation of Schiff's bases :

$$PhN_3 + Ph_2CS \longrightarrow N_2 + S + Ph_2C:NPh$$

Since Schiff's bases are readily hydrolysed to the component amine and ketone, the reaction constitutes a new and easy means of passage from an azide to the corresponding amine (for other methods of effecting the same transformation, see Forster and Fierz,

* Part XXIV, *Ber.*, 1933, **66**, 1932.

J., 1908, **93**, 1859; Freudenberg, *Ber.*, 1933, **65**, 1183; Wienhaus, *ibid.*, p. 1461; Bertho and Maier, *Annalen*, 1932, **495**, 113).

Study of the reaction has so far been confined to its end-products; the intermediate stages must therefore remain uncertain. Two possibilities present themselves : (*a*) combination of the thioketone and azide in molecular proportion with subsequent elimination of elementary nitrogen and sulphur; (*b*) combination of a free radical of the type $CH_2Ph\cdot N$: (cf. Curtius, *J. pr. Chem.*, 1930, **125**, 305, 308) with the thioketone, followed by elimination of sulphur :

$$PhN_3 + Ph_2CS \longrightarrow \begin{array}{c} Ph_2\!\!\diagdown \\ PhN\text{--}N \end{array}\!\!\!>\!\!N \longrightarrow Ph_2C\colon\!NPh + S + N_2 \quad . \quad . \quad . \quad (a)$$

$$CH_2Ph\cdot N\colon + Ph_2CS \longrightarrow \begin{array}{c} Ph_2C\text{--}N\cdot CH_2Ph \\ \diagdown S \diagup \end{array}\!\!\! \longrightarrow Ph_2C\colon\!N\cdot CH_2Ph + S \quad . \quad . \quad (b)$$

The reaction has been applied to phenyl-, benzyl-, α-naphthyl-, and benzenesulphon-azides together with thiobenzophenone, pp'-dimethoxythiobenzophenone, and xanthione; the products have been identified with Schiff's bases prepared from the corresponding amines and keto-chlorides.

EXPERIMENTAL.

Benzophenone and Phenylazide.—Attempts to effect interaction between benzophenone and phenylazide were made by heating the components together (*a*) at 115—120° for 5 hours, (*b*) at 140—145° for 6 hours, and (*c*) at 170°. Experiments (*a*) and (*b*) led to the recovery of unchanged benzophenone only; in experiment (*c*) the mixture exploded.

Thiobenzophenone and Phenylazide.—Thiobenzophenone (6 g.) and phenylazide (3·6 g.) were heated together at about 110° in a stream of nitrogen; dissolution of the thioketone occurred with deep blue coloration and was followed by brisk evolution of gas and change of colour to red in the course of 2 hours. The cooled reaction product was drained on a tile and crystallised from alcohol, forming leaflets, m. p. and mixed m. p. with phenyliminodiphenyl-methane (Pauly, *Annalen*, 1877, **187**, 199), 116—117°.

pp'-Dimethoxythiobenzophenone and Phenylazide.—pp'-Dimethoxythiobenzophenone (2·6 g.) (Schönberg, *Ber.*, 1928, **61**, 1375) and phenylazide (4·5 g.) were caused to interact as described above. The excess of phenylazide (3·2 g.) was removed by steam distillation, and the residue drained on a tile. The crystals were extracted with a little cold chloroform and the solution was filtered from sulphur. Evaporation of the chloroform left a residue, which after two recrystallisations from ligroin formed light yellow leaflets, m. p. 95° (unchanged on admixture with authentic phenyliminodianisylmethane).

Xanthione and Phenylazide.—Xanthione (2·1 g.) (cf. Schönberg, Schütz, and Nickel, *Ber.*, 1928, **61**, 1328) and phenylazide (4·5 g.) were heated together in a stream of nitrogen at 110°. After 4 hours, when the initially dark green solution had become red and evolution of nitrogen had ceased, the excess of phenylazide (3·3 g.) was removed by distillation in a vacuum. The residue was extracted several times with dry ether, the extract being decanted from undissolved sulphur and evaporated; after several recrystallisations from light petroleum the product formed golden-yellow needles, m. p. 134—135°, identical with phenyliminoxanthen (cf. Graebe and Röder, *Ber.*, 1899, **32**, 1689) (Found : C, 84·4; H, 4·9; N, 5·3. Calc. for $C_{19}H_{13}ON$: C, 84·2; H, 4·8; N, 5·2%). We also prepared this compound by the interaction of aniline and 9 : 9-dichloroxanthen (Schönberg und Schütz, *Annalen*, 1927, **454**, 51).

pp'-Dimethoxythiobenzophenone and α-Naphthylazide.—pp'-Dimethoxythiobenzophenone (2·6 g.) and α-naphthylazide (5 g.) (Forster and Fierz, *J.*, 1907, **91**, 1945) were heated together in an oil-bath (about 120°) for 2 hours. The excess of naphthylazide was removed by distillation in a vacuum. The residue was extracted with a little cold dry ether and the solution after filtration from sulphur was concentrated to crystallisation. After several recrystallisations from light petroleum there were obtained 2·5 g. of yellow leaflets, m. p. 133—134° (unchanged on admixture with the product of interaction of α-naphthylamine and dianisyldichloromethane).

pp'-Dimethoxythiobenzophenone and Benzylazide.—pp'-Dimethoxythiobenzophenone (2·6 g.) and benzylazide (5 g.) (Curtius and Ehrhardt, *Ber.*, 1922, **55**, 1559) were heated together for 2¼ hours at 100°. By working as in the previous experiments, 2·9 g. of crude product were obtained which after several recrystallisations from light petroleum formed light yellow leaflets, m. p. 93° (Found : C, 79·65; H, 6·3; N, 4·1. Calc. for $C_{22}H_{21}O_2N$: C, 79·8; H, 6·3; N,

4·2%). The product was identical with the Schiff's base prepared from benzylamine and dianisyldichloromethane (cf. Schönberg and Urban, *Ber.*, 1934, **67**, 1999).

Xanthione and Benzenesulphonazide.—A solution of xanthione (1·05 g.) and benzenesulphon-azide (1 g.) in xylene (4 c.c.) was boiled for 2 hours with exclusion of atmospheric moisture. After removal of the solvent the residue was freed from sulphur by extraction with cold dry ether, the ethereal solution evaporated in a vacuum, and the residue crystallised once from alcohol and twice from light petroleum, yielding golden-yellow leaflets (1 g.), m. p. 165—166°, of *benzenesulphonimidoxanthen*, $O<^{C_6H_4}_{C_6H_4}>C:N\cdot SO_2Ph$ (Found C, 68·0; H, 4·2; N, 4·3; S, 9·85. $C_{19}H_{13}O_3NS$ requires C, 68·0; H, 3·9; N, 4·2; S, 9·6%).

The above product (1 g.) was hydrolysed by boiling with alcohol (25 c.c.) and 4% sodium hydroxide solution (10 c.c.) for 3 hours. On cooling, and addition of water, 0·56 g. of xanthone separated (theo., 0·57 g.). The filtrate from the xanthone was neutralised to litmus with hydrochloric acid and concentrated in a vacuum. The benzenesulphonamide which separated amounted to 0·49 g. (theo., 0·5 g.).

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122. *The Caryophyllenes. Part II.*

By G. R. RAMAGE and J. L. SIMONSEN.

IN Part I (*J.*, 1934, 1806) we showed Semmler's liquid " caryophyllenic acid " to be a mixture of two crystalline acids, *d-cis*-caryophyllenic acid, $C_9H_{14}O_4$, m. p. 80—81°, and *d-cis*-norcaryophyllenic acid, $C_8H_{12}O_4$, m. p. 125—127°, the latter acid being converted by appropriate reactions into an unsaturated acid, dehydronorcaryophyllenic acid, $C_8H_{10}O_4$, m. p. 193°. These observations have been fully confirmed by the recent investigations of Ruzicka and Zimmermann (*Helv. Chim. Acta*, 1935, **18**, 219). Our anticipation that an examination of the oxidation products of dehydronorcaryophyllenic acid would throw light on the structure of the parent acid has been realised.

When the unsaturated acid is oxidised with ozone in ethyl acetate or in sodium carbonate solution, it yields a keto-acid, which is extremely hygroscopic and cannot be purified. Analyses of four crystalline derivatives, the *phenylsemicarbazone*, decomp. 165°, the p-*nitrophenylhydrazone*, decomp. 192°, and two 2 : 4-*dinitrophenylhydrazones*, decomp. 243° and 215—217°, show it to have the composition $C_7H_{10}O_5$. On further oxidation with hydrogen peroxide in alkaline solution it gives *as.*-dimethylsuccinic acid.

These results receive their simplest interpretation if *d-cis*-norcaryophyllenic acid is *d-cis*-3 : 3-dimethyl*cyclo*butane-1 : 2-dicarboxylic acid (I); dehydronorcaryophyllenic acid will then be 3 : 3-dimethyl-Δ^1-*cyclo*butene-1 : 2-dicarboxylic acid (II), and the keto-acid * either α-keto-ββ-dimethylglutaric acid (IV) or α'-keto-αα-dimethylglutaric acid (V) formed from the primary oxidation product, αδ-diketo-ββ-dimethyladipic acid (III) by the action of the hydrogen peroxide generated during the decomposition of the ozonide.

$$Me_2C-CH\cdot CO_2H \quad Me_2C-C\cdot CO_2H \quad Me_2C\cdot CO\cdot CO_2H \quad Me_2C\cdot CO\cdot CO_2H \quad Me_2C\cdot CO_2H$$
$$H_2C-CH\cdot CO_2H \quad H_2C-C\cdot CO_2H \quad H_2C\cdot CO\cdot CO_2H \quad H_2C\cdot CO_2H \quad H_2C\cdot CO\cdot CO_2H$$
$$\text{(I.)} \qquad\qquad \text{(II.)} \qquad\qquad \text{(III.)} \qquad\qquad \text{(IV.)} \qquad\qquad \text{(V.)}$$
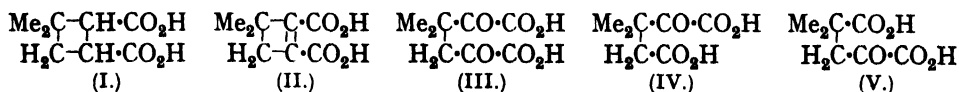
An attempt was made to isolate the diketo-acid (III) by decomposing the ozonide with

* [Note added, April 1st.] By the courtesy of Dr. E. H. Farmer we have been able to compare this acid with α-keto-ββ-dimethylglutaric acid. The *p*-nitrophenylhydrazone of the latter, decomp. 158°, is not identical with the *p*-nitrophenylhydrazone, decomp. 192°, of the oxidation acid, which must therefore be (V).

hydrogen in the presence of palladium–norit (compare Fischer, Düll, and Ertel, *Ber.*; **1932**, **65**, 1467), but only derivatives of the monoketo-acid could be obtained.

The constitution of norcaryophyllenic acid suggested tentatively by Ruzicka and Zimmermann (*loc. cit.*) is thus confirmed.

Our previous tacit assumption that caryophyllenic and norcaryophyllenic acids belong to a homologous series has now been proved experimentally. Bromocaryophyllenic acid was converted by silver oxide in aqueous solution into hydroxycaryophyllenic acid or, more probably, the lactonic acid, and this, without purification, was oxidised successively with lead peroxide and potassium permanganate (compare Baeyer, *Ber.*, 1896, **29**, 1907), *d*-cis-norcaryophyllenic acid being obtained. It follows, therefore, that caryophyllenic acid must be either (VI) or (VII).

(VI.) $\quad$ Me$_2$C—CH·CH$_2$·CO$_2$H $\qquad$ Me$_2$C—CH·CO$_2$H
$\qquad\quad$ H$_2$C—CH·CO$_2$H $\qquad\qquad$ H$_2$C—CH·CH$_2$·CO$_2$H $\quad$ (VII.)

The observation of Ruzicka, Bardhan, and Wind (*Helv. Chim. Acta*, 1931, **14**, 423), that the tetramethylglycol prepared from methyl caryophyllenate by the action of methyl-magnesium iodide yields ααα′α′-tetramethylglutaric acid on oxidation, obviously involves a molecular rearrangement which is more readily explicable on the basis of (VII) than of (VI). It does not, however, appear possible to decide between these two formulæ by analytical methods and we are undertaking the synthesis of this acid and also of norcaryophyllenic acid.

During the purification of dehydronorcaryophyllenic acid (see below) we isolated in small quantity an optically inactive *acid*, $C_8H_{12}O_4$, m. p. 148—149°, which is in all probability *dl*-cis-norcaryophyllenic acid, the active acid having racemised during the treatment with bromine. This acid is identical possibly with the acid having a similar melting point described by Ruzicka and Zimmermann (*loc. cit.*).

Considerable evidence regarding the structure of the caryophyllenes is now available, although interpretation is difficult, and we prefer to defer discussion until we have completed our experiments on the oxidation of dihydro-β-caryophyllene (*loc. cit.*, p. 1808).

It was thought at first that the oxidation product of dehydronorcaryophyllenic acid had the composition $C_5H_8O_3$, and a number of new derivatives of dimethylpyruvic acid were prepared. Dimethylpyruvic acid is obtained most conveniently by the method briefly described by Perkin and Simonsen (*Proc.*, 1909, **25**, 164).

EXPERIMENTAL.

Dehydronorcaryophyllenic Acid and dl-cis-*Norcaryophyllenic Acid.*—For the preparation of the former acid the conditions previously described were followed, except that it was found more convenient to effect the bromination at 140° instead of 120°. After hydrolysis with alcoholic potassium hydroxide and removal of the alcohol, acidification deposited dehydronor-caryophyllenic acid (0·9 g. from 2 g. of norcaryophyllenic acid); the filtrate was extracted with ether and after removal of the solvent an oil was obtained which on treatment with concentrated hydrochloric acid gave a further quantity (0·2 g.) of the unsaturated acid. The methyl ester was an oil which crystallised when cooled in a freezing mixture. The hydrochloric acid mother-liquors gave on concentration an acid (0·5 g.), m. p. 140°, raised to 145—147° by crystallisation from water. Since the acid was not stable to permanganate, it was dissolved in alkali and treated with this reagent until the colour was permanent (ice). The recovered *acid* (0·3 g.) now crystallised from water in rosettes of needles, m. p. 148—149°, and was optically inactive in acetone solution (Found : C, 56·0; H, 7·1; *M*, 171. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%; *M*, 172). By treatment with acetyl chloride a liquid anhydride was obtained which was readily hydrolysed by hot water to the parent acid, m. p. 148—149°.

Oxidation of Dehydronorcaryophyllenic Acid with Ozone.—(i) *In sodium carbonate solution.* The acid (0·6 g.) in sodium carbonate solution (10 c.c.; Na$_2$CO$_3$, 0·2 g.) (ice) was treated with ozone until the solution was stable to potassium permanganate. After acidification and saturation with ammonium sulphate, the solution was extracted with ether (10 times), and the dried extract evaporated; an oil (0·42 g.) remained which crystallised when kept over sulphuric acid but liquefied rapidly in the air. The keto-acid (IV or V) gave a faint colour

with ferric chloride and did not reduce Fehling's solution. On admixture with an aqueous sulphuric acid solution of 2 : 4-dinitrophenylhydrazine a dinitrophenylhydrazone (A) separated; the filtrate slowly deposited a second dinitrophenylhydrazone (B) in long needles. The 2 : 4-*dinitrophenylhydrazone A* crystallised from alcohol in yellow needles, decomp. 243°, unaltered by two further crystallisations (Found : C, 44·6; H, 4·1. $C_{13}H_{14}O_6N_4$,$\frac{1}{4}C_2H_5$·OH requires C, 44·5; H, 4·5%). The 2 : 4-*dinitrophenylhydrazone B* crystallised from dilute alcohol in yellow prisms, decomp. 215—217° (Found : C, 44·4; H, 4·2%). In one experiment the acid was kept with a dilute alcoholic solution of the dinitrophenylhydrazine sulphate for some weeks; a third hygroscopic 2 : 4-*dinitrophenylhydrazone C*, m. p. 132°, was then obtained in pale yellow needles [Found : (air-dried) N, 13·2; H_2O, 18·4; (dried in a low vacuum) C, 43·6; H, 4·5. $C_{13}H_{14}O_6N_4$,$4\frac{1}{2}H_2O$ requires N, 12·9; H_2O, 18·6%. $C_{13}H_{14}O_6N_4$ requires C, 44·1; H, 4·0%].

(ii) *In ethyl acetate.* The acid (0·5 g.) in ethyl acetate (15 c.c.) was ozonised for 2·5 hours at 0°. After removal of the ethyl acetate in a vacuum, the ozonide was kept over-night with water (0·5 c.c.) and then heated on the water-bath for 1 hour. The two dinitrophenylhydrazones A and B referred to above were prepared and the former was analysed (Found : C, 44·3, 44·5; H, 4·2; 4·1; N, 14·6. $C_{13}H_{14}O_6N_4$,$\frac{1}{4}C_2H_5$·OH requires C, 44·5; H, 4·5; N, 14·8%). The p-*nitrophenylhydrazone* crystallised from dilute alcohol in small yellow needles, decomp. 192° (Found : C, 50·5; H, 4·8; N, 13·3. $C_{13}H_{15}O_5N_3$ requires C, 50·5; H, 4·9; N, 13·6%). The *phenylsemicarbazone* separated from dilute alcohol in prismatic needles, decomp. 165°. This derivative is somewhat difficult to purify, since it tends to separate as an oil (Found : C, 54·5; H, 5·7. $C_{14}H_{17}O_5N_3$ requires C, 54·7; H, 5·5%).

Oxidation of the Keto-acid (IV or V) *with Hydrogen Peroxide.*—To the acid (0·3 g.) in sodium hydroxide solution, hydrogen peroxide (100 vol.; 1 c.c.) was added and after 1 hour the mixture was heated on the water-bath for a further hour. The cooled acidified solution was saturated with ammonium sulphate and extracted with ether; evaporation of the solvent from the extract left a crystalline solid (0·23 g.), decomp. 139°. The acid crystallised from water in prismatic needles, decomp. 139—140°, both alone and after admixture with as.-dimethylsuccinic acid (Found : C, 49·6; H, 6·6. Calc. : C, 49·3; H, 6·9%).

Conversion of d-cis-*Caryophyllenic Acid into* d-cis-*Norcaryophyllenic Acid.*—Caryophyllenic acid (10 g.) and phosphorus pentachloride (22 g.) were heated on the water-bath and after $\frac{1}{4}$ hour bromine (12 g.) was gradually added. After completion of the reaction the acid chloride was poured on ice, and the bromo-acid extracted with ether. Removal of the solvent gave an oil (14·2 g.), which was dissolved in water (150 c.c.) and, after the addition of silver oxide (25 g.), kept at 80° for 3 hours. The dried silver salt was suspended in ether and warmed with methyl iodide (25 g.) for 1 hour. The filtered solution gave, after the removal of the ether, an oil, which yielded on distillation a fraction (*A*), b. p. 138—142°/17 mm. (1·8 g.), and a high-boiling residue (*B*) (2 g.). From the original aqueous filtrate from the silver salt, an acid (*C*) (5 g.) was isolated by extraction of the acidified solution with ether. For the preparation of norcaryophyllenic acid, (*B*) was dissolved in warm aqueous sodium hydroxide, and the solution acidified and extracted with ether; after removal of the solvent the residual oil was dissolved in water (20 c.c.) and acetic acid (5 c.c.) and warmed on the water-bath, and lead peroxide (6 g.) added. When effervescence had ceased, the solution was filtered, the excess of lead removed with sulphuric acid, and the filtered solution made alkaline with aqueous sodium carbonate. Potassium permanganate solution (2·5%) was added (mechanical stirring) until the colour was permanent; the boiled and filtered solution was made acid to Congo-paper with hydrochloric acid and evaporated to dryness. The residual salts were extracted with ether, which left on evaporation a gum (1·5 g.). This was dissolved in cold water.(charcoal), and a little insoluble resin thus removed. After removal of the water, the residue was dissolved in hot benzene and decanted from the insoluble gum, and the benzene evaporated; an oil remained which crystallised on being stirred with hydrochloric acid. The solid, m. p. 123—125°, was crystallised from benzene and then had m. p. 125—127°, both alone and after admixture with d-cis-norcaryophyllenic acid (Found : C, 55·7; H, 6·8. Calc. : C, 55·8; H, 7·0%). This acid was obtained also from the ester (*A*) after hydrolysis. In this case lead tetra-acetate was used in place of lead peroxide and the yield was inferior. The acid (*C*) contained much unchanged caryophyllenic acid, and norcaryophyllenic acid could not be isolated from it after oxidation.

2-*Phenyl*-4-iso*propylideneoxazolone.*—A mixture of hippuric acid (powdered to pass a 40-mesh sieve; 48 g.), acetone (120 g.), acetic anhydride (90 g.), and freshly fused sodium acetate (24 g.) was heated under reflux at 110° for 6 hours. In the early stages of the reaction a pasty

solid separated, which slowly redissolved, yielding a pink solution. The solid which separated when the cooled solution was poured into a large volume of water was collected, washed with aqueous sodium carbonate to remove benzoic acid, and recrystallised from alcohol, the *oxazolone* being obtained in needles, m. p. 99—100° (Found : C, 71·4; H, 5·4. $C_{18}H_{11}O_2N$ requires C, 71·6: H, 5·5%).

α-Benzamido-ββ-dimethylacrylic Acid.—The oxazolone (1 g.) was mixed with aqueous potassium hydroxide solution (KOH, 0·5 g.) and heated on the water-bath for 1 hour. The sparingly soluble potassium salt that separated was decomposed with hydrochloric acid. The *acrylic acid* obtained crystallised from ethyl acetate–ether in fine needles, decomp. 217° (Found : C, 65·7; H, 5·8; N, 6·8; *M*, 218. $C_{12}H_{13}O_3N$ requires C, 65·7; H, 5·9; N, 6·4%; *M*, 219). The acrylic acid results also when the oxazolone is hydrolysed with baryta or cold concentrated hydrochloric acid.

Dimethylpyruvic Acid.—The oxazolone (18 g.), dissolved in concentrated hydrochloric acid (100 c.c.), was heated on the water-bath for 6 hours. In the early stages of the reaction a granular precipitate separated, which redissolved, crystallisation of benzoic acid following. The cooled solution was filtered, and the filtrate extracted with ether. Evaporation of the solvent left dimethylpyruvic acid, b. p. 65°/14 mm. (Found : C, 51·9; H, 7·3. Calc. : C, 51·7; H, 6·9%). In agreement with Craig (*J. Amer. Chem. Soc.*, 1934, **56**, 2008; compare Perkin and Simonsen, *loc. cit.*) the phenylhydrazone was found to have m. p. 152°. The *phenylsemicarbazone*, long needles from dilute alcohol, had m. p. 137° (Found : N, 17·0. $C_{12}H_{15}O_2N_3$ requires N, 16·9%); the p-*nitrophenylhydrazone* crystallised from dilute alcohol in bright yellow needles, which became buff-coloured when dried at 100°; m. p. 155° (Found : N, 16·8. $C_{11}H_{13}O_4N_3$ requires N, 16·7%); the 2 : 4-*dinitrophenylhydrazone* separated from dilute alcohol in yellow needles, m. p. 194—195° (Found : C, 44·3; H, 4·3. $C_{11}H_{12}O_6N_4$ requires C, 44·6; H, 4·1%).

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123. *Mercury Derivatives of Camphor. Part II.*

By JAMES D. LOUDON.

THE successful application of Peters' reaction (*Ber.*, 1905, **38**, 2567), *viz.*,

$$R{\cdot}SO_2H + HgCl_2 \longrightarrow R{\cdot}HgCl + SO_2 + HCl$$
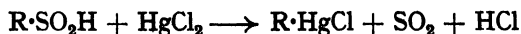
to the preparation of camphor-10-mercurichloride (Part I, J., 1933, 823) has led to investigation of other camphorsulphinic acids as sources of the related mercury derivatives. The results now obtained reveal marked differences in the reactivities of these acids towards mercuration. Thus, 3-chloro- and 3-bromo-camphor-10-sulphinic acids reacted with mercuric chloride to give yields of the corresponding mercury derivatives which were distinctly lower than that obtained from the unhalogenated acid under the same conditions. Considerable improvement has been effected by the use of pyridine as reaction medium or by employing the aqueous alkali sulphinates instead of the free acid (cf. "Organic Syntheses," III, p. 99)—both modifications being designed to protect the mercurated products from the attack of mineral acids formed in the reaction, and the former yielding slightly better results. On the other hand, 3-chloro- and 3-bromo-camphor-π-sulphinic acids, although much less stable than their "10" sulphinic analogues from the point of view of preservation, were so resistant to mercuration that evolution of sulphur dioxide was not perceptible and, at best, mere traces of mercurated products resulted. The investigation of these π-derivatives has consequently been abandoned.

The halogenated camphor-10-mercurichlorides were more stable than the parent substance to reduction by alkaline stannite solution, but their conversion into symmetrical mercury derivatives was readily accomplished by the action of copper gauze in pyridine (cf. Hein, Wagler, and Retter, *Ber.*, 1925, **58**, 1499).

EXPERIMENTAL.

3-Chlorocamphor-10-*sulphinic Acid*.—3-Chlorocamphor-10-sulphonyl chloride (10 g.) was shaken for 3 hours with a concentrated solution of sodium sulphite (30 g. of the hydrate) and ice (20 g.). After precipitation by concentrated sulphuric acid the product separated from alcohol–chloroform in small compact crystals, m. p. 157° (decomp.) markedly affected by the rate of heating (Found : Cl, 14·3. $C_{10}H_{15}O_3ClS$ requires Cl, 14·2%).

3-Bromocamphor-10-*sulphinic acid* was prepared and purified in a similar way : m. p. 165° (decomp.) (Found : Br, 27·2. $C_{10}H_{15}O_3BrS$ requires Br, 27·1%).

3-Chlorocamphor-π-sulphinic acid was most conveniently prepared by adding the sulphonyl chloride in small quantities to a hot aqueous solution of sodium sulphite. After acidification of the cooled solution the product was obtained as a fine white powder, which melted with decomposition and could not be satisfactorily crystallised (Found : Cl, 14·0. $C_{10}H_{15}O_3ClS$ requires Cl, 14·2%).

3-Bromocamphor-π-sulphinic acid, prepared in the same way, had similar properties; m. p. 149° (decomp.) (Found : Br, 26·9. $C_{10}H_{15}O_3BrS$ requires Br, 27·1%).

3-Chlorocamphor-10-*mercurichloride*.—3-Chlorocamphor-10-sulphinic acid (9 g.) was refluxed with mercuric chloride (18 g.) in pyridine (30 c.c.) for 3 hours. The cooled solution, freed from metallic mercury, was cautiously added to an excess of dilute hydrochloric acid and the precipitate was collected, washed (finally with alcohol), dried, and extracted (Soxhlet) with chloroform, from which, on cooling, the pure compound separated in long needles, m. p. 218—219°. Yield, 40—50% of the theoretical $[\alpha]_{5461}^{16°} \pm 0·0°$ ($c = 1·24$ in pyridine), $+ 5·0°$ ($c = 1·00$ in chloroform) (Found : Hg, 47·3. $C_{10}H_{14}OCl_2Hg$ requires Hg, 47·5%).

Bis-3-*chlorocamphor*-10-*mercury*.—Copper gauze (5 g.) was kept in a solution of 3-chloro-camphor-10-mercurichloride (5 g.) in pyridine (30 c.c.) in a stoppered flask for 24 hours. After removal of the pyridine under reduced pressure, the semi-solid residue was shaken with con-centrated aqueous ammonia and finally washed with water. The straw-coloured product was purified from alcohol–chloroform and then had m. p. 175°; $[\alpha]_{5461}^{16°} - 22·8°$ ($c = 1·14$ in pyridine) (Found : Hg, 35·2. $C_{20}H_{28}O_2Cl_2Hg$ requires Hg, 35·1%).

Treatment of acetone solutions of the compound with mercuric halides gave the correspond-ing mercurihalides, which were purified from alcohol–chloroform.

3-Chlorocamphor-10-*mercuribromide*, needles, m. p. 176° (Found : Hg, 43·1. $C_{10}H_{14}OClBrHg$ requires Hg, 43·1%), and *3-chlorocamphor*-10-*mercuri-iodide*, needles, m. p. 184° (Found : Hg, 39·1. $C_{10}H_{14}OClIHg$ requires Hg, 39·1%), were also prepared by shaking the mercurichloride at the ordinary temperature with bromine (iodine) in aqueous potassium bromide (iodide) solution.

Similar methods were employed for the corresponding 3-bromocamphor-10-mercury deriv-atives. *3-Bromocamphor*-10-*mercurichloride* was obtained from the sulphinic acid (pyridine) in 30—35% yields : m. p. 232°, $[\alpha]_{5461}^{16°} + 44·8°$ ($c = 1·07$ in pyridine) (Found : Hg, 43·3. $C_{10}H_{14}OBrClHg$ requires Hg, 43·1%). *Bis*-3-*bromocamphor*-10-*mercury* melted at 188—189° after crystallisation from acetone; $[\alpha]_{5461}^{16°} + 29·13°$ ($c = 1·03$ in pyridine) (Found : Hg, 30·4. $C_{20}H_{28}O_2Br_2Hg$ requires Hg, 30·4%). *3-Bromocamphor*-10-*mercuribromide* had m. p. 195° (Found : Hg, 39·5. $C_{10}H_{14}OBr_2Hg$ requires Hg, 39·3%), and *3-bromocamphor*-10-*mercuri-iodide* m. p. 173° (Found : Hg, 36·4. $C_{10}H_{14}OBrIHg$ requires Hg, 36·0%).

Replacement of Mercury by Halogens.—A suspension of 3-chlorocamphor-10-mercurichloride in an aqueous solution of bromine and potassium bromide was warmed until the solid was converted into a heavy oil. The latter was extracted with chloroform; after being freed from bromine, the concentrated extract yielded 3-chloro-10-bromocamphor, m. p. 98° (Arm-strong and Lowry, J., 1902, 81, 1452, give m. p. 98°).

3 : 10-Dibromocamphor (αβ-dibromocamphor), m. p. 114° (lit. 114°), was prepared in a similar way.

3-Chloro-10-*iodocamphor*.—The mercurichloride (1 g.) was refluxed for ¼ hour with iodine (1 g.) in benzene (30 c.c.). After removal of the excess of iodine by washing with sulphite and carbonate solutions the crystalline deposit from the concentrate separated from alcohol in colourless needles, m. p. 89° (Found : C, 38·3 ; H, 4·6. $C_{10}H_{14}OClI$ requires C, 38·4 ; H, 4·5%).

3-Bromo-10-*iodocamphor*, similarly prepared, melted at 88—89° (Found : C, 33·7 ; H, 4·1. $C_{10}H_{14}OBrI$ requires C, 33·6 ; H, 3·9%).

124. 2 : 4-Dinitrodiphenylsulphones.

By JAMES D. LOUDON.

A STUDY of the properties of 2 : 4-dinitrodiphenylsulphones has revealed some interesting examples of their reactivity, of which the following is a preliminary account. Their preparation has been effected by extension of Ullmann and Pasdermadjian's original procedure (*Ber.*, 1901, **34**, 1150), *e.g.*, condensation of (I) and (II), or by the modification in which (II) is replaced by 2 : 4-dinitrophenyl-*p*-toluenesulphonate. The facility with which the reaction proceeds suggested the possibility of forming polysulphones, *e.g.*, (V) by nitration of (III), followed by condensation with a second molecule of (I).
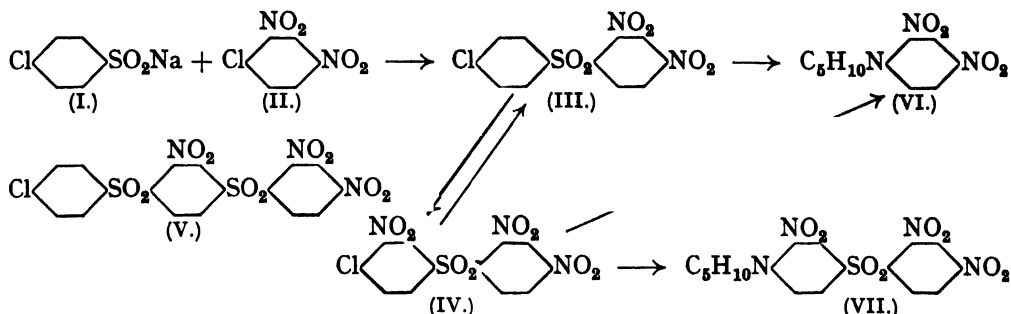
The mononitration of (III) proceeded smoothly and the product was submitted to the piperidine test for reactive halogen, following the procedure of Le Fèvre and Turner (J., 1927, 1113). The difficulty of obtaining a homogeneous product, together with the ultimate isolation of (VI), showed that under these conditions (excess of piperidine) rapid scission of the sulphone linkage occurs. This was further demonstrated by the smooth conversion of other 2 : 4-dinitrodiphenylsulphone derivatives (*e.g.*, III) into (VI), the reaction being analogous to the slower replacement of the phenylsulphonyl group in *o*-nitrodiphenylsulphone by aniline (Levi and Smiles, J., 1932, 1488). That piperidine, however, exerts a preferential attack on the halogen of (IV) is shown by the isolation of (VII) from the reaction conducted in dioxan with the theoretical amount of base.

The mobility of the arylsulphonyl group in these compounds also frustrated the attempt to prepare (V) by interaction of (I) and (IV), the sole result being regeneration of (III), apparently by exchange of arylsulphonyl anions. The following table summarises the results obtained in other cases, the sign + denoting completion, and − failure of the reaction in which, with the exceptions noted, three molecular proportions of sulphinate were employed.

R.	R'.		R.	R'.	
Ethyl	Methyl *	+	Phenyl	Ethyl	+
Methyl	Ethyl	+	Phenyl	2 : 5-Dichlorophenyl	−
Ethyl	*p*-Tolyl *	+●	*p*-Chlorophenyl	Phenyl	+
p-Tolyl	Ethyl	+	*p*-Chloro-*m*-nitrophenyl	*p*-Chlorophenyl	+
p-Tolyl	Phenyl †	+	*p*-Bromo-*m*-nitrophenyl	*p*-Bromophenyl	+
Phenyl	*p*-Tolyl	+	*m*-Nitrophenyl	*p*-Tolyl	+
Phenyl	Methyl	+	*p*-Chloro-*m*-nitrophenyl⁻	*m*-Nitrophenyl	−
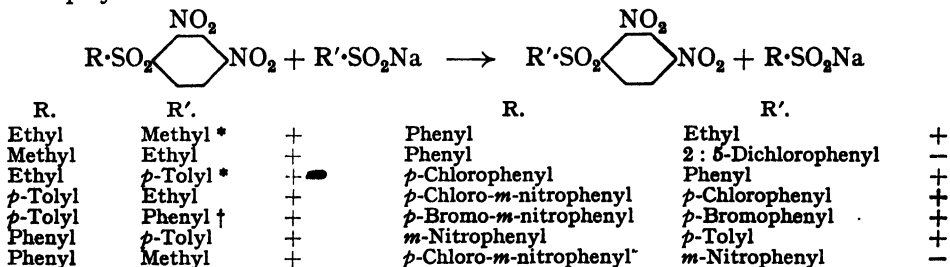
* Large excess. † 12 Molecules.

The table includes only those examples in which the nature of the isolated substance was clearly established by melting point and mixed melting point observations. In several other cases (*e.g.*, R = phenyl, R' = *p*-chlorophenyl) the product was obviously a mixture (qualitative halogen test), which resisted fractionation from acetic acid.

The results recorded suffice to indicate in a qualitative manner that the reaction is

N N

influenced (*a*) by the concentration of free sulphinate ion and (*b*) by the relative stabilities of the competing anions (actual and potential). They offer some points of contrast to the work of Gibson (J., 1931, 2637; 1932, 1819, *et seq.*), who has recently demonstrated sulphonyl mobility in the following case, and records failure of the exchange process (1)

$$R \cdot SO_2 \cdot \underset{\underset{\displaystyle S \cdot CH_3}{|}}{C}H \cdot CO \cdot CH_3 \quad \underset{\overset{\displaystyle R \cdot SO_2 \cdot S \cdot CH_3}{\longleftarrow}}{\overset{R' \cdot SO_2 \cdot S \cdot CH_3}{\longrightarrow}} \quad R' \cdot SO_2 \cdot \underset{\underset{\displaystyle S \cdot CH_3}{|}}{C}H \cdot CO \cdot CH_3$$
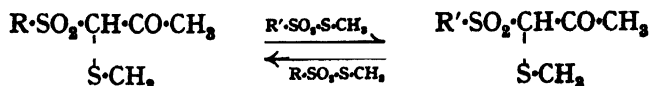
when purely aromatic thiolsulphonic esters (*e.g.*, $Ph \cdot SO_2 \cdot SPh$ as distinct from $Ph \cdot SO_2 \cdot S \cdot CH_3$) are employed and (2) where replacement of arylsulphonyl by alkylsulphonyl is attempted. With sulphones of the present series these limitations do not apply, for, on the one hand, both types of disulphoxide in presence of carbonate produced a facile exchange and, on the other, the effected replacement of arylsulphonyl by sodium alkylsulphinates was less readily reversed.

Experiments are in progress on the exchange of the sulphone group when attached to other cationoid centres, such as in thiolsulphonic esters.

EXPERIMENTAL.

Preparation of 2 : 4-Dinitrodiphenylsulphones.—2 : 4-Dinitrochlorobenzene (or 2 : 4-dinitrophenyl *p*-toluenesulphonate) and the requisite sodium sulphinate in molecular proportion were heated in aqueous alcoholic solution for 10—20 minutes. After cooling, the solid was collected, washed with alcohol and water, and crystallised from acetic acid. The compounds, phenyl (159—160°), *p*-tolyl (187°), *o*-tolyl (154°), *p*-chlorophenyl (168°), *p*-bromophenyl (190°), methyl (187°), and ethyl (157°) -2 : 4-dinitrophenylsulphones, had the uncorrected melting points indicated, the values being in close agreement with those recorded for the same substances formed by oxidation of the corresponding sulphides (*J. Amer. Chem. Soc.*, 1932, **54**, 1985; 1933, **55**, 4956). 2 : 4 : 3'-*Trinitrodiphenylsulphone* had m. p. 196—197° (Found : N, 11·8. $C_{12}H_7O_6N_3S$ requires N, 11·9%), and 2' : 5'-*dichloro*-2 : 4-*dinitrodiphenylsulphone*, m. p. 178° (Found : N, 7·5. $C_{12}H_6O_6N_2Cl_2S$ requires N, 7·4%).

4'-Chloro-2 : 4 : 3'-Trinitrodiphenylsulphone.—A solution of potassium nitrate (1·01 g.) in 20 c.c. of concentrated sulphuric acid was added to 4'-chloro-2 : 4-dinitrodiphenylsulphone (3·42 g.) in 60 c.c. of concentrated sulphuric acid. The crystals formed on standing were recrystallised from acetic acid and had m. p. 203° (Found : N, 10·9. $C_{12}H_6O_6N_3ClS$ requires N, 11·1%).

4'-Bromo-2 : 4 : 3'-trinitrodiphenylsulphone.—The product of the nitration of 4'-bromo-2 : 4-dinitrodiphenylsulphone, conducted as above, had m. p. 210° after several crystallisations from acetic acid (Found : N, 9·9. $C_{12}H_6O_6N_3BrS$ requires N, 10·0%).

Action of Piperidine.—The reaction (0·2 g. of sulphone and 2 c.c of piperidine) was rapid even in the cold. After being warmed for a few minutes, the solution was cooled and treated with dilute acid; the precipitated oil rapidly became solid except in the cases of 4'-chloro (and bromo)-2 : 4 : 3'-trinitrodiphenylsulphones, where partial solidification occurred only after several weeks. After crystallisation from alcohol the product in each case was identified as 2 : 4-dinitropiperidinobenzene, m. p. and mixed m. p. 92°.

2 : 4 : 3'-*Trinitro*-4'-*piperidinodiphenylsulphone.*—4'-Chloro-2 : 4 : 3'-trinitrodiphenylsulphone (0·5 g.; 1 mol.) in 5 c.c. of dioxan was treated with piperidine (0·22 g.; 2 mols.) in 2 c.c. of dioxan, and the resulting orange solution kept for 12 hours. The crystalline deposit was identified as piperidine hydrochloride (m. p. and mixed m. p. 236°). The oil formed by addition of water to the filtrate was extracted with concentrated hydrochloric acid. The extract on dilution with water yielded a solid which crystallised from acetone–alcohol in yellow plates, m. p. 190—191° (Found : N, 13·0. $C_{17}H_{16}O_8N_4S$ requires N, 12·8%). The same piperidine derivative was formed from the corresponding bromotrinitrodiphenylsulphone.

Sulphonyl Exchange.—The following example is typical of the procedure employed. Dinitrodiphenylsulphone (0·5 g.), dissolved in 6 c.c. of warm dioxan, was treated with a hot solution of sodium *p*-toluenesulphinate (0·9 g.) in 2 c.c. of water. The homogeneous mixture was heated for a few minutes and cooled (prolonged or more drastic treatment leads to complications which are under investigation). The solid which separated was washed with alcohol and then with water; it melted crude at 179—181°; crystallised from acetic acid, it had m. p. 187—188°, unaffected by admixture with 2 : 4-dinitrophenyl-*p*-tolylsulphone (m. p. 187°).

Action of Disulphoxides.—*p*-Tolyl *p*-toluenethiolsulphonate (0·3 g.) and 2 : 4-dinitrodiphenyl-sulphone (0·3 g.), dissolved in hot dioxan, were treated with a small amount of sodium carbonate and a few drops of water. The product, isolated as above, yielded 2 : 4-dinitrophenyl-*p*-tolyl-sulphone (m. p. and mixed m. p. 185—186°).

Methyl *p*-toluenethiolsulphonate gave the same result, but in the absence of alkali carbonate no reaction occurred in either case.

The author acknowledges his indebtedness to Mr. A. Naismith, B.Sc., who prepared some of the sulphones, and also to the Chemical Society for a grant.

NOTES.

Electrolytic Reduction of αα'-Dicyano-ββ-dimethylglutarimide. By G. GRATTON and G. R. RAMAGE.

As a preliminary to the preparation of bridged piperidonecarboxylic acids, which appeared likely to prove of value as a starting point for the synthesis of substituted *cyclo*butane acids, the electrolytic reduction of αα'-dicyano-ββ-dimethylglutarimide was investigated. This gave in poor yield the *lactam* of δ-*amino-αγ-dicyano-ββ-dimethylvaleric acid*, from which by heating with hydrochloric acid a substance was obtained having the properties of a pyridinecarboxylic acid. This was probably the *monoamide* of 6-*hydroxy-2 : 4-dimethylpyridine-3 : 5-dicarboxylic acid*, hydrolysis being accompanied by dehydrogenation and the wandering of a methyl group to the α-position in the pyridine nucleus. Since attempts to prepare the normal hydrolysis product failed, this method of synthesis was abandoned.

αα'-Dicyano-ββ-dimethylglutarimide (4 g.) in ethyl alcohol (70 c.c.) and concentrated sulphuric acid (7 c.c.) was reduced with a rotating lead cathode (5 amps.; 125 sq. cm. immersed) for 8 hours, the cell being cooled with ice. The cathode liquid was added to water (500 c.c.), and the precipitated unchanged imide (3 g.) recovered. The free acid was exactly neutralised with potassium hydroxide, and the solution evaporated to dryness. The residue was extracted with alcohol (Soxhlet), and on removal of the solvent a gum remained which crystallised when rubbed with water. The *lactam* crystallised from alcohol–benzene in prisms, m. p. 194° (Found : C, 60·7; H, 6·3; N, 23·5. $C_9H_{11}ON_3$ requires C, 61·0; H, 6·2; N, 23·7%). The lactam (3 g.) and concentrated hydrochloric acid (20 c.c.) were heated in a sealed tube for 5 hours at 130—140°; the resulting amic *acid* crystallised from hot water, in which it was very sparingly soluble, in thin plates, decomp. above 360° (Found : C, 51·7; H, 5·0; N, 13·6. $C_9H_{10}O_4N_2$ requires C, 51·4; H, 4·8; N, 13·3%). It was insoluble in all the ordinary organic solvents, lost ammonia when digested with alkali, and gave a red colour with aqueous ferric chloride.

Substituted Phenyldihydroresorcinols. By L. E. HINKEL, E. E. AYLING, and J. F. J. DIPPY.

THE requisite intermediate substituted benzylideneacetones were obtained by the following general procedure : *o*-Chlorobenzaldehyde (20 c.c.), acetone (50 c.c.), 10% aqueous sodium hydroxide (20 c.c.), and water (500 c.c.) were shaken together for 24 hours, and the mixture was then saturated with sodium chloride. Ether extracted a liquid (17 g.), b. p. 160—163°/17 mm., which solidified in a freezing mixture and crystallised from well-cooled light petroleum (b. p. 40—60°) in stout colourless needles, m. p. 24·5° (Found : Cl, 19·3. Calc. : Cl, 19·7%) (Vorländer, *Annalen*, 1897, **294**, 291, describes *o*-chlorobenzylideneacetone as a liquid, b. p. 189°/30 mm.).

δ-o-Chlorophenyldihydroresorcinol.—Molecular proportions of *o*-chlorobenzylideneacetone (24 g.), ethyl malonate, and sodium ethoxide in alcohol were condensed by heating on a water-bath for 10 hours. The subsequent procedure, similar to that described for δ-*iso*propyldi-

hydroresorcinol by Crossley and Pratt (J., 1915, **107**, 173), yielded *5-o-chlorophenyldihydro-resorcinol* (8 g.; 27%), which crystallised from aqueous alcohol in fine white plates, m. p. 149° (decomp.) (Found : Cl, 15·7. $C_{13}H_{11}O_3Cl$ requires Cl, 16·0%).

5-o-Methoxyphenyldihydroresorcinol.—*o*-Methoxybenzylideneacetone (20 g., prepared in 68% yield by the above procedure) was condensed as described above, but with heating for 12 hours. Acidification of the dihydroresorcylic acid yielded an oil, which solidified on cooling, the solution also depositing a small quantity of crystals, and crystallisation from aqueous alcohol gave *5-o-methoxyphenyldihydroresorcinol* in colourless prisms, m. p. 145° (Found : C, 71·7; H, 6·4. $C_{13}H_{14}O_3$ requires C, 71·6; H, 6·4%).

5-p-Methoxyphenyldihydroresorcinol.—*p*-Methoxybenzylideneacetone (37 g., prepared in 72% yield by the above procedure) was condensed as described above, but with heating for 9 hours, to yield *5-p-*methoxyphenyldihydroresorcinol (27 g., 59%), which crystallised from acetone in fine colourless leaflets and from alcohol in colourless prisms, m. p. 175° (decomp.) (Vorländer and Erig, *Annalen*, 1897, **294**, 310, record m. p. about 185°) (Found : C, 71·1; H, 6·4. Calc. : C, 71·6; H, 6·4%).

Note on " The Conductivity of Methoxides and Ethoxides." By W. F. K. WYNNE-JONES.

IN a paper with the above title (J., 1934, 1197) Jones and Hughes reported the results of careful measurements on the conductivity of methoxides, ethoxides, and methyl and ethyl carbonates in their respective alcohols. Their results are in good agreement with the data published by the author (*J. Physical Chem.*, 1927, **31**, 1647) for the conductivity of sodium methoxide and methyl carbonate in methyl alcohol, as is shown below.

NaOMe : $\Lambda = 98·4 - 236c^{1/2}$ (J. and H.); $\Lambda = 98·3 - 223c^{1/2}$ (W.-J.).
NaMeCO$_3$: $\Lambda = 91·0 - 277c^{1/2}$ (J. and H.); $\Lambda = 90·5 - 265c^{1/2}$ (W.-J.).

In their discussion of the solvent correction, Jones and Hughes state : " Wynne-Jones has corrected conductivity data for sodium methoxide in methyl alcohol on the assumption that the carbon dioxide concentration can be calculated from the conductivity of the solvent." Actually, the correction was applied for both strong and weak bases quite empirically, and for strong bases such as sodium methoxide the equation used (see p. 1656) was $\Lambda_{obs.} = (1 - x)\Lambda_{true} + x\Lambda_{NaMeCO_3}$, which is identical with that deduced by Jones and Hughes (p. 1202).

The author also outlined a more general empirical method of correcting the conductivity data for strong acids and bases, using the equation $\Lambda_{obs.} = \Lambda_0 - bc^{1/2} + k/c$, which, as indicated elsewhere (Wynne-Jones, *J. Amer. Chem. Soc.*, 1932, **54**, 2130), can be applied to data for aqueous solutions.

With regard to Jones and Hughes's statement that " it has been found that ammonia is present in quantities of the order of $2 \times 10^{-7}N$," it seems that this is an hypothesis rather than an experimental fact. In order to account for a specific conductivity of 10^{-7} ohm^{-1}, it would be necessary to assume an ammonia concentration of $1 \times 10^{-6}N$: for reasons already discussed by the author, the presence of such amounts of ammonia in the methyl alcohol used by Goldschmidt and Hartley and their students is improbable.—FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY. [*Received, January 18th, 1935.*]

ANNUAL GENERAL MEETING

THE ninety-fourth Annual General Meeting was held on March 28th, the President, Professor G. T. MORGAN, O.B.E., D.Sc., LL.D., F.R.S., occupying the Chair.

The notice summoning the meeting was read, and the President formally presented the Report of Council for 1934—1935, together with the Balance Sheets and Statements of Accounts for 1934.

The Treasurer, on being called upon by the President, dealt with the accounts in detail, and stated that the extra revenue from annual subscriptions and other sources had been insufficient to meet the increased cost of the *Journal* and *Abstracts*. He pointed out that during the last two years the Society had spent £1440 in excess of its income, and that if this loss were to continue for any length of time the investments of the Society would be seriously depleted with corresponding diminution of income.

He referred to the scheme of co-operation between the three principal chemical organisations, and expressed the hope that the steps taken would assist the Society eventually to place its finances on a firm footing, as the proposed agreement provides for a more equitable distribution of some of the heavy charges hitherto borne by this Society.

In conclusion, he thanked the officials and members of the staff for the efficient manner in which they had carried out their duties during an exceptionally busy period.

REPORT OF COUNCIL, 1934—1935.

IN addition to the formal reports under the customary headings, the Council wishes to direct the attention of Fellows to certain matters of special importance.

A notable advance has been made during the year in the negotiations for closer co-operation between organisations of chemists. Reference was made in last year's report to a draft scheme for the formation of a Chemical Council. By agreement between the three Chartered Societies concerned a " Provisional Chemical Council " was appointed to elaborate the draft scheme and define its financial implications; the Council consisted of three representatives each from the Chemical Society, the Institute of Chemistry, and the Society of Chemical Industry, together with three representatives from industry. The Provisional Council has submitted a report which has been accepted in general principle by the Councils of the constituent bodies, with certain minor amendments. The scheme is now being put into proper legal form by the Provisional Chemical Council, after which it will be laid before the Councils of the constituent bodies for their final consideration.

The scheme of lectures and discussions outside London continues to develop, and during the year under review 29 such meetings were held. The Council again congratulates the Local Representatives on the success of their efforts, and thanks them and other Fellows who have contributed to the success of these meetings.

The number of Fellows again shows a small increase. The number of new elections has maintained the higher level reached last year, and the number of removals is notably less. At the same time, it must be noted that the cost of the Society's publications shows a progressive increase, largely due to an increased number of pages in the *Journal*. The Council would urge on all Fellows the need for continued efforts to increase the number of Fellows. The loss during the economic depression was large, and it should be the immediate aim of the Society to regain a membership of 4000 Fellows as soon as possible.

I. *Fellowship Statistics.*

The number of Fellows on December 31st, 1933, was 3620. During 1934, 218 Fellows were elected and 16 reinstated, compared with 235 and 13, respectively, in 1933. The Society has lost 50 Fellows by death, 101 by resignation, and 75 by removal for non-payment of annual subscriptions; the corresponding figures in 1933 were 53, 83, and 100, respectively.

The number of Fellows at December 31st, 1934, was 3628; of whom 134 pay the reduced annual subscription. The net increase in number of Fellows in the year was, therefore, 8; in 1933 an increase of 12 was recorded and in 1932 a decrease of 167.

II. *Honorary Fellows.*

The Council regrets to record that during the year the Society has lost by death four of its Honorary Fellows, Professor Camille Matignon on March 18th, Madame Marie Curie on July 4th, Professor Emanuele Paternò on January 17th, and Professor Bohuslav Brauner on February 15th. An obituary notice of Professor Matignon is being prepared by Sir William J. Pope, and Dr. A. S. Russell has accepted the Council's invitation to deliver the Marie Curie Memorial Lecture. These memorials will be published in the *Journal.*

The number of Honorary Fellows is now 33.

III. *Jubilee Fellows.*

The congratulations of the Society have been conveyed to Mr. A. J. Greenaway and to Mr. H. H. B. Shepherd, who on April 2nd and May 21st, respectively, completed 60 years of Fellowship.

Congratulations have also been sent to the following who attained their jubilee as Fellows during the year :

	Elected.
William D. Borland	April 17th, 1884.
Arthur G. Perkin	April 17th, 1884.
H. Brereton Baker	June 19th, 1884.
William T. Burgess	June 19th, 1884.
John Hargreaves	June 19th, 1884.
Frederick J. Down	November 20th, 1884.
Herbert John Hodges	December 18th, 1884.
Sir Herbert Jackson, K.B.E.	December 18th, 1884.
Jason H. Worrall	December 18th, 1884.
J. Norman Collie	February 5th, 1885.
Augustus E. Dixon	February 5th, 1885.
Arthur G. Green	February 5th, 1885.
George G. Henderson	February 5th, 1885.

IV. *Journal.*

The *Journal* for 1934, containing 2019 pages (366 pages more than the *Journal* for 1933), consists of 443 memoirs (1906 pages), 35 notes (20 pages), 2 lectures (19 pages), a report on atomic weights (14 pages), the Presidential Address (9 pages), the report of the Annual General Meeting (13 pages), and Obituary Notices (38 pages).

During 1934, 504 papers were received, of which 8 were declined. Of the 443 memoirs published, 154 deal with General, Physical, and Inorganic Chemistry, and 289 with Organic Chemistry.

The average interval between the receipt and the publication of the papers in 1934 was 9·5 weeks; the corresponding interval for the 388 memoirs and 26 notes published in 1933 was 9·4 weeks.

Nomenclature of the Isotopes of Hydrogen.

In April the Council appointed a Committee, consisting of Professor C. K. Ingold, Professor T. S. Moore, Professor E. K. Rideal, Dr. N. V. Sidgwick, and the Editor, to consider proposals received from the American Chemical Society regarding the nomenclature of the isotopes of hydrogen and of compounds containing them. An interim report has been sent to the American Chemical Society and further discussions are proceeding.

V. *Bureau of Chemical Abstracts.*

Two Meetings of the Bureau were held during the year.

Abstracts. The appended table shows the number and average length of the abstracts in Sections " A " and " B " published during 1934, the figures for 1933 being included for comparison.

| | Abstracts A. | | | | Abstracts B. | | | |
| | 1933. | | 1934. | | 1933. | | 1934. | |
	No. of Abs.	Pages.	No. of Abs.	Pages.	No. of Abs.	Pages.	No. of Abs.	Pages.
1st quarter	3,619	330	3,586	338	3,212	270	3,714	286
2nd ,, ...	3,454	324	3,946	372	2,952	256	3,486	272
3rd ,, ...	3,534	336	3,653	340	3,441	272	3,716	288
4th ,, ...	3,833	354	3,896	372	3,539	290	3,409	272
	14,440	1,344	15,081	1,422	13,144	1,088	14,325	1,118
Average length per abstract ...	0·19 Col.		0·19 Col.		0·17 Col.		0·16 Col.	

The 15,081 "A" abstracts comprised 6929 in General, Physical, and Inorganic Chemistry, 405 in Geochemistry, 2823 in Organic Chemistry, and 4924 in Biochemistry. The corresponding figures for 1933 were 6646, 425, 2849, and 4524.

Of the 14,325 "B" abstracts, 7025 were from journal literature and 7300 were abstracts of Patents (in 1933 : 6840 and 6304 respectively).

The continued increase in the number of abstracts published is an inevitable consequence of the world-wide expansion in scientific investigation and literature. The most notable increases have been in the section of Biochemistry in the " A " abstracts and in the Patents in the " B " abstracts.

The Bureau was gratified to learn that the Biochemical Society had made a donation to the Chemical Society in appreciation of the work being done in publishing abstracts of Biochemical papers.

Annual Index. The joint Annual Index of the abstracts for 1933 covered 640 pages, as compared with 578 pages for the 1932 Index. The cost of printing the Index was £1248 6s. 9d. and of the paper £244 3s. 4d. (corresponding figures for the 1932 Index were £1148 2s. 8d. and £227 12s. 5d.).

The total number of entries in the Index increased from 84,600 to 87,675 in 1933.

Decennial Index. The Names volumes of the Decennial Index, 1923—1932, covering 2101 pages, were issued in March 1934. Work on the Subjects Index is approaching completion, and it is hoped to issue the volume by about the end of March 1935.

The number of completed subscriptions received for the Index up to the end of 1934 was 693; in addition, deposits have been paid on 110 copies, but the balance of the amounts is not yet forthcoming.

The Bureau is glad to be able to report that the subscriptions received up to the beginning of December, together with the amounts already contributed, or promised, by the Chemical Society, the Society of Chemical Industry, and the Royal Society, will be sufficient to cover the costs of the whole work, including the printing of the Subjects Index.

It has been decided to include in the Subjects Index a statement showing the method of numbering the more important homocyclic and heterocyclic compounds according to Richter's system.

VI. *Library.*

Excluding the attendances on evenings devoted to meetings of the Chemical Society, there were 8549 attendances during the year, as compared with 8399 in 1933. Of these 5367 were made by Fellows of the Chemical Society, and 3182 by Members of Contributing Societies, as against 3050 in 1933.

The number of books borrowed was 5525, against 5518 in the previous year; of these 1345 were issued by post, compared with 1284 in the preceding year.

The Library telephone facilities continue to be extensively used, and the incoming calls included 758 inquiries which necessitated reference to books in the Library.

The additions to the Library comprise :

(1) A valuable bequest by the late Colonel Sir Frederic Nathan, K.B.E., of 557 books, 73 volumes of periodicals and 457 pamphlets relating to explosives, firearms, etc.
(2) 197 books, of which 81 were presented; 674 volumes of periodicals and 255 pamphlets; as against 216 books, 692 volumes of periodicals, and 245 pamphlets last year.

The total number of volumes added during the year was 1501, showing an increase of 593. The Library now contains 38,810 volumes consisting of 11,817 books and 26,993 bound volumes of periodicals.

VII. *General.*

Vacancies on Council.

Two vacancies on Council have occurred during the year, caused by the retirement of Professor A. J. Allmand, and of Mr. H. S. Patterson. . The Council expressed its appreciation of their services, and in April appointed Professor G. I. Finch as an Ordinary Member of Council until the next Annual General Meeting.

Lectures in London.

Three special Lectures have been held in London during the year : On April 19th, Lord Rutherford of Nelson lectured on " The Periodic Law of Mendeléeff and its Interpretation " at the Royal Institution, the meeting being held to commemorate the Centenary of the birth of Mendeléeff; on October 18th, Professor P. M. S. Blackett gave a lecture on " Induced Radioactivity " at the Royal Institution, and on February 14th the Fifth Liversidge Lecture on " The Process of Coagulation in Smoke " was delivered by Professor R. Whytlaw-Gray at the Institution of Mechanical Engineers.

Lectures outside London.

Eighteen Lectures have been delivered outside London, and, in addition, Fellows were invited to attend the five Bedson Lectures at Armstrong College, Newcastle-on-Tyne.

Birmingham. At the University, Edgbaston; March 5th, on " Recent Work in Molecular Structure," by Dr. N. V. Sidgwick; November 5th, on " The Development of Chemical Kinetics," by Mr. C. N. Hinshelwood; January 29th, on " Surface Reactions," by Professor E. K. Rideal.

Bristol. At the University; February 15th, on " The Properties and Chemistry of Heavy Hydrogen," by Dr. L. Farkas.

Edinburgh. At the University; October 22nd, on " The Molecular Structure of the Carbohydrates," by Professor W. N. Haworth.

Liverpool. At the University; March 13th, on " The Experimental Study of Some Gas Reactions," by Professor M. W. Travers; January 25th, on " Some Researches on Long Chain Compounds," by Dr. J. C. Smith.

Manchester. At the University; February 23rd, on " Chlorophyll," by Professor Dr. Hans Fischer.

Newcastle and Durham. Bedson Lectures at Armstrong College; March 2nd, on " Elements, Old and New," by Professor J. Kendall; May 18th, on " Gutta Percha, Balata, and Caoutchouc," by Professor G. G. Henderson; October 26th, on " Some Aspects of Photochemical Change," by Professor A. J. Allmand; December 7th, on " Some Problems of Stereochemistry," by Dr. W. H. Mills, and February 8th, on " The Biochemistry of the Thyroid Gland," by Professor C. R. Harington.

North Wales. At University College, Bangor; March 9th, on "Film Reactions," by Professor E. K. Rideal; November 16th, on "Science and the Oil Industry," by Mr. W. H. Cadman; November 26th, on "A General View of Polysaccharide Structure," by Professor W. N. Haworth; January 18th, on "Alchemy and the Alchemists," by Professor J. Read.

St. Andrews and Dundee. At the University, St. Andrews; January 11th, on "Some Problems in Relation to Complex Metallic Salts," by Dr. F. G. Mann; February 15th, on " Orientation of Substitutions in the Benzene Series," by Professor R. Robinson.

Sheffield. At the University; March 15th, on "Some Stereochemical Problems," by Dr. W. H. Mills; February 1st, on "Some Recent Developments in the Study of Chemical Reaction Mechanism," by Mr. C. N. Hinshelwood.

South Wales. At the University College, Swansea; March 12th, on "Some Families of Plant Products," by Professor R. Robinson; January 21st, on "Isothermal Sol-Gel Transformation, or Thixotropy," by Professor Dr. H. Freundlich.

Discussions in London.

Four Discussions were held : May 3rd, on "Unicellular Chemistry," opened by Dr. J. Vargas Eyre; June 7th, on "Chemical Syntheses under Pressure," when papers were read by Mr. R. Taylor, Dr. D. V. N. Hardy, and Dr. D. D. Pratt; November 15th, on "Chemical Problems in Agricultural Science," opened by Sir John Russell; and February 7th, on "Intermetallic Compounds," opened by Professor C. H. Desch.

The discussion on "Chemical Syntheses under Pressure" was held by invitation of the President at the Chemical Research Laboratory of the Department of Scientific and Industrial Research at Teddington, and Fellows were conducted over the extensive laboratories.

Discussions outside London.

Three discussions were held :

Liverpool. November 3rd, on "Teaching of Chemistry," opened by Mr. S. V. Brown, Chairman of the Science Masters' Association Committee.

Manchester. November 9th and 10th, on "Applications of X-Rays and Spectroscopy to the Elucidation of Chemical Structure." Papers were read by the following : Professor W. L. Bragg, Mr. W. T. Astbury, Mr. J. M. Robertson, Dr. E. G. Cox, Professor T. M. Lowry, Professor I. M. Heilbron, Mr. A. E. Gillam, Dr. C. P. Snow, Dr. J. W. Cook, Dr. J. M. Gulland, and Dr. R. A. Morton. On November 9th a party of Fellows visited the Shirley Institute by invitation of the Director, Dr. R. H. Pickard.

Sheffield. At the University; November 15th on "The Surface of Glass," opened by Professor W. E. S. Turner.

Ordinary Scientific Meetings.

Of Ordinary Scientific Meetings for the communication of papers eight were held in London, one in Manchester (January 24th), and one in Newcastle (October 19th).

Representatives of the Society on other Bodies.

Bureau of Chemical Abstracts	Mr. F. P. Dunn, Mr. A. J. Greenaway, Dr. J. T. Hewitt, Professor S. Sugden, and the Treasurer.
Federal Council for Chemistry	Sir William J. Pope, Professor S. Sugden, and Professor J. F. Thorpe.
Technical Committee of the Divisional Chemical Council of the British Standards Institution which has taken over the work of the Dairy Research Committee of the Empire Marketing Board	Mr. A. L. Bacharach.

In addition, the President *ex officio* is a member of the Council and of the Executive Committee of the City and Guilds of London Institute.

Ordinary Members of Council (Town).—Prof. J. W. Cook, Prof. G. I. Finch, and Dr. J. J. Fox.

Ordinary Members of Council (Country).—Mr. W. A. S. Calder, Prof. T. P. Hilditch, Dr. F. G. Mann, and Prof. J. Read.

A vote of thanks to the Scrutators, proposed by Prof. J. Read and seconded by Dr. L. Hunter, was acknowledged by Mr. E. Hinks.

The President then delivered his address entitled " Recent Researches on Certain of the Rarer Elements."   At the conclusion of the address, a vote of thanks to the President for his services and for his address was proposed by Prof. A. G. Green, seconded by Prof. C. S. Gibson, and carried enthusiastically; the President briefly replied.

In accordance with a newly established custom, the induction of the new President did not take place at the Annual General Meeting, being postponed until the Anniversary Dinner held in the evening.

INCOME AND EXPENDITURE GENERAL PURPOSES ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1934.

Income.

Expenditure.

INCOME AND EXPENDITURE ACCOUNTS OF OTHER FUNDS FOR THE YEAR ENDED 31ST DECEMBER, 1934.

PUBLICATIONS FUND.

Income.

Expenditure.

INCOME AND EXPENDITURE ACCOUNTS OF OTHER FUNDS FOR THE YEAR ENDED 31ST DECEMBER, 1934.

LIBRARY.

1933	Income	1934
£ s. d.		£ s. d.
	To Donations:—	
100 0 0	Association of British Chemical Manufacturers	100 0 0
21 0 0	Biochemical Society	21 0 0
10 10 0	Faraday Society	15 15 0
50 0 0	Institute of Brewing	25 0 0
250 0 0	Institute of Chemistry	250 0 0
100 0 0	Society of Chemical Industry	100 10 0
10 10 0	Society of Dyers and Colourists	10 10 0
21 0 0	Society of Public Analysts	21 0 0
—	Sir Fratulis C. Bay	3 3 0
—	Birmingham Dinner Committee	23 4 10
543 0 0		569 9 10
7 13 5	„ Miscellaneous receipts	3 17 8
1909 19 2	„ Contribution from General Purposes Account	1825 12 1
£2180 11 7		£2398 19 7

1933	Expenditure	1934
£ s. d.		£ s. d.
1325 10 9	By Salaries and Wages	1335 14 11
187 7 0	„ Superannuation of Library Staff	167 7 0
696 6 6	„ Books and Periodicals*	615 5 7
130 5 0	„ Binding	133 17 8
70 4 10	„ Printing, Stationery and Postages (proportion)	46 12 3
91 15 4	„ House Expenses, etc. (proportion)	103 7 8
9 2 2	„ Miscellaneous	16 15 0
£2480 11 7		£2398 19 7

* Other than those received in exchange.

RESEARCH FUND.

1933	Income	1934
£ s. d.		£ s. d.
467 4 7	To Dividends on Investment	477 16 8
155 14 10	„ Income Tax recovered	155 14 9
63 8 7	„ Repayment of Grants	79 15 9
15 16 8	„ Grants not applied for	—
1 18 6	„ Interest on Deposit	3 13 5
£703 3 2		£716 0 7

1933	Expenditure	1934
£ s. d.		£ s. d.
616 10 0	By Grants	672 8 0
40 0 0	„ Longstaff Medallists, Honoraria	—
4 0 0	„ Longstaff Medals	—
21 0 0	„ Hugo Müller Lecturer, Honorarium	—
5 10 0	„ Miscellaneous Expenses	7 3 10
16 3 2	„ Balance, being Excess of Income over Expenditure, carried to Balance Sheet	36 8 9
£703 3 2		£716 0 7

SPECIAL PUBLICATIONS FUND.

1933	Income	1934
£ s. d.		£ s. d.
14 0 6	To Sales of Publications:— Abstracts "A" printed on one side of the paper	55 0 0
8 16 0	Memorial Lectures, Vol. I.	9 9 6
7 17 1	Do. Vol. II.	7 18 5
10 9 1	Do. Vol. III.	17 19 6
7 13 1	List of Fellows	4 11 0
4 19 8	Portraits	4 5 1
4 11 8	Faraday Lectures	8 6 1
16 10	Perkin Memorial Volume	1 16 6
—	Discussion Number	10 0 0
—	Fourth Pedler Lecture	6 3 0
114 18 1	„ Dividend on Investment	113 12 10
55 10 6	„ Interest on Deposit	56 9 1
1 17 1	„ Income Tax recovered	2 6 3
18 10 2	„ Balance, being Excess of Expenditure over Income, carried to Balance Sheet	18 10 2
27 4 8		—
£217 17 6		£190 18 4

1933	Expenditure	1934
£ s. d.		£ s. d.
6 6 6	By Advertising, etc.	57 1 0
53 12 9	„ Production of Abstracts "A", printed on one side of the paper	—
125 4 6	„ Do. List of Fellows	—
16 19 9	„ Do. Memorial Lectures, Vol. III.	—
—	„ Reprints for Memorial Lectures, Vol. IV.	8 8 5
—	„ Do. of Fourth Pedler Lecture	—
—	„ Balance, being Excess of Income over Expenditure, carried to Balance Sheet	125 8 11
£217 17 6		£190 18 4

SPECIAL LECTURES FUND.

Income.

1933				1934		
£ s. d.				£ s. d.		
24 7 9	To Dividends on Investments	...	...	24 13 8		
11 7 11	" Income Tax recovered	...	...	11 7 3		
—	" Interest on Deposit	...	...	7 7 3		
—	" Balance, being Excess of Expenditure over Income, carried to Balance Sheet	...	...	18 5		
£45 17 5				£47 6 6		

Expenditure.

1933				1934		
£ s. d.				£ s. d.		
—	By Honorarium	...	...	25 0 0		
—	" Lecture Expenses	...	...	22 6 6		
45 17 5	" Balance, being Excess of Income over Expenditure, carried to Balance Sheet	...	...	—		
£45 17 5				£47 6 6		

STAFF PENSIONS FUND.

Income.

1933				1934		
£ s. d.				£ s. d.		
77 10 1	To Transfer from General Purposes Account	...	...	76 14 8		
51 17 6	" Dividends on Investments	...	...	33 13 10		
10 12 5	" Income Tax recovered	...	...	10 12 6		
£120 0 0				£120 0 0		

Expenditure.

1933				1934		
£ s. d.				£ s. d.		
120 0 0	By Pension paid during 1934	...	...	120 0 0		
£120 0 0				£120 0 0		

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

Income.

1933				1934		
£ s. d.				£ s. d.		
39 16 9	To Dividends on Investments	...	...	40 8 9		
13 11 0	" Income Tax recovered	...	...	12 11 0		
13 13 0	" Interest on Deposit	...	...	14 9		
108 15 7	" Balance, being Excess of Expenditure over Income carried to Balance Sheet	...	...	—		
£166 16 0				£53 14 6		

Expenditure.

1933				1934		
£ s. d.				£ s. d.		
150 0 0	By Harrison Prize	...	...	—		
6 16 0	" Harrison Plaque	...	...	—		
—	" Balance, being Excess of Income over Expenditure, carried to Balance Sheet	...	...	53 14 6		
£166 16 0				£53 14 6		

THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31st December, 1934.

GENERAL PURPOSES.

Liabilities.

1933			1934			
£ s. d.		£ s. d.		£ s. d.		
954 5 5	To Subs. received in advance	892 13 0				
3,029 19 11	" Sundry Creditors (Printing and other Expenses)					
35 0 0	" Sale of Library Books	3,255 12 0				
36 1 6	" Suspense Account					
	" Excess of Assets over Liabilities as per last Balance Sheet	23,675 9 9				
24,683 2 2	*Add* Profit on Sale of £403 13s. 10d. Transvaal 3% Guar. Stock ...	—				
6 19 4						
24,690 1 6						
400 0 0	*Deduct* Transfer to Suspense Account toward Cost of Renewal of the Electric Lighting Installation	—				
24,290 1 6						
614 11 9	" Excess of Expenditure over Income for Year	835 1 10				
23,675 9 9		23,350 7 11				
—	*Add* Transfer from Suspense Account unexpended balance	33 1 6				
—		23,383 9 5				
£27,730 16 7		£27,081 14 5				

Assets.

1933				1934		
£ s. d.				£ s. d.		
25,884 6 1	By Investments as per Schedule (cost or value when acquired)	...	...	25,884 6 1		
741 16 4	" Sundry Debtors	...	...	445 4 4		
175 0 0	" Subscriptions in Arrear, £569 4s. 3d. Estimated to realise	...	...	350 0 0		
759 15 3	" Cash in hand and at Bank	...	...	380 19 7		
£27,730 16 7				£27,081 14 5		

PUBLICATIONS FUND.

Liabilities.

1933			1934			
£ s. d.		£ s. d.				
11,162 13 8	To Excess of Assets over Liabilities as per last Balance Sheet	11,119 10 11				
	Add Amount transferred from Income and Expenditure Account for Investment	155 10 0				
206 10 0						
21,419 3 8						
299 12 9	*Less* Loss on Shares Sold	—				
11,119 10 11		11,275 0 11				
£11,119 10 11		£11,275 0 11				

Assets.

1933				1934		
£ s. d.				£ s. d.		
8 7 1	By Amount due from General Purposes	...	...	11,229 3 10		
11,018 3 10	" Investments as per Schedule (cost or value when acquired)	...	...	45 17 1		
93 0 0	" Cash at Bank	...	...	—		
£11,119 10 11				£11,275 0 11		

THE CHEMICAL SOCIETY. BALANCE SHEETS, 31ST DECEMBER, 1934.

RESEARCH FUND.

Liabilities.	1933		1934		Assets.	1933		1934
	£ s. d.		£ s. d.		By Investments as per Schedule (cost or value when acquired)	£ s. d.		£ s. d.
To Sundry Creditors	616 10 0		710 8 0			14,443 2 0		14,443 2 0
„ Excess of Assets over Liabilities as per last Balance Sheet	14,481 5 11	14,447 9 1			„ Cash at Bank	620 17 1		751 3 10
Add Excess of Income over Expenditure for year	16 3 2	36 8 9		14,483 17 10				
	14,447 9 1							
	£15,063 19 1		£15,194 5 10			£15,063 19 1		£15,194 5 10

SPECIAL PUBLICATIONS FUND.

Liabilities.		1934		Assets.	1933		1934
To Amount prepaid for 1935	30 0 0	35 0 0		By Investment as per Schedule (cost or value when acquired)	1600 0 0		1600 0 0
„ Sundry Creditors	9 13 2	15 5 6		„ Sundry Debtors	3 11 6		— — —
„ Sinking Fund for Collective Index (1923–32) as per last Balance Sheet	700 3 10	557 2 9		„ Cash at Bank	789 1 4		683 16 8
Add Transfer from General Purposes	250 0 0						
Interest	6 18 11	4 2 7					
		561 5.					
Less Paid on Account to Bureau of Chemical Abstracts	957 2 9	250 0 0	311 5 4				
	400 0 0						
	557 2 9						
Excess of Assets over Liabilities as per last Balance Sheet	1833 1 7	1795 16 11					
Less Excess of Expenditure over Income for year	37 4 8						
	1795 16 11						
Add Excess of Income over Expenditure for Year		125 8 11	1921 5 10				
	£2392 12 10		£2288 16 8			£2392 12 10		£2288 16 8

SPECIAL LECTURES FUND.

Liabilities.		1934		Assets.	1933		1934
To Excess of Assets over Liabilities as per last Balance Sheet	1090 10 4	1076 7 9		By Investments as per Schedule (cost or value when acquired)	1000 0 0		1000 0 0
Add Excess of Income over Expenditure for year	17 5			„ Cash at Bank	76 7 9		75 9 4
Less Excess of Expenditure over Income for year		18 5	1075 9 4				
	1076 7 9						
	£1076 7 9		£1075 9 4			£1076 7 9		£1075 9 4

STAFF PENSIONS FUND.

Liabilities.		Assets.	1933		1934
To Excess of Assets over Liabilities as per last Balance Sheet	907 14 0	907 14 0	By Investments as per Schedule (cost or value when acquired)	902 13 9		902 13 9
			„ Cash at Bank	5 0 3		5 0 3
	£907 14 0			£907 14 0		£907 14 0

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

Liabilities.		1934		Assets.	1933		1934
To Excess of Assets over Liabilities as per last Balance Sheet	1199 6 11	1165 11 4		By Investments as per Schedule (cost or value when acquired)	1101 7 11		1101 7 11
Add Excess of Income over Expenditure for year		53 14 6			„ Cash at Bank	64 3 5		117 17 11
Less Excess of Expenditure over Income for year	103 15 7						
	1165 11 4		1219 5 10				
	£1165 11 4		£1219 5 10			£1165 11 4		£1219 5 10

SCHEDULE OF INVESTMENTS.

GENERAL PURPOSES.

Nominal Details.	Cost or Value when Acquired. £ s. d.	Market Value 31st December, 1934. £ s. d.
£787 London, Midland and Scottish Railway 4% Debenture Stock	839 3 7	853 17 8
£1520 14s. 2d. Cardiff Corporation 3% Stock, 1914/54	1550 0 0	1530 14 3
£1400 India 2½% Stock	1316 1 0	1163 0 0
£2400 Bristol Corporation 2½% Debenture Stock, Bristol Dock Account	2070 2 0	2256 0 0
£2713 London, Midland and Scottish Railway 4% Preference Stock	3572 1 0	2360 6 2
£1200 Leeds Corporation 3% Stock	1143 0 4	1164 2 0
£1098 6s. 2d. Union of South Africa 3% Stock, 1954/64	1087 12 10	1113 15 0
£1200 London and North Eastern Railway 3% Debenture Stock	1035 11 0	1090 0 0
£700 Canada 2½% Stock, 1950/60	704 8 6	707 0 0
£3529 6s. 9d. 3% Conversion Loan, 1944/64	3446 0 2	3130 0 1
£1100 5% ditto ditto	1045 0 2	1361 5 0
£500 4% Funding Loan, 1960/90	480 0 2	723 0 0
£11,212 9s. 3½% Conversion Stock 1961, or after	8487 2 2	12,445 16 4
	£25,854 5 1	£29,816 15 6

PUBLICATIONS FUND.

Nominal Details.	Cost or Value when Acquired. £ s. d.	Market Value 31st December, 1934. £ s. d.
£8974 19s. 9d. 3½% Conversion Stock, 1961, or after	5300 13 8	7743 4 8
£5173 1s. 6d. 5% Conversion Loan, 1944/64	3199 18 7	3926 13 7
£817 P. & O. Steam Navigation Co. Deferred Stock	3060 0 0	714 17 6
£803 London, Midland and Scottish Railway 4% Guaranteed Stock	457 12 7	633 3 0
	£11,018 2 10	£13,016 18 9

RESEARCH FUND.

Nominal Details.	Value or Cost when Acquired. £ s. d.	Market Value 31st December, 1934. £ s. d.
£1000 London and North Eastern Railway 4% 2nd Guaranteed Stock	1010 0 0	905 0 0
£1084 Great Western Railway 2½% Debentures	1049 18 11	796 3 7
£1142 16s. New South Wales 3% Stock, 1935	1000 0 0	1149 18 10
£1122 Metropolitan Water Board 3% "B" Stock	1002 16 9	1110 15 7
£1483 London, Midland and Scottish Railway 4% Debenture Stock	1508 0 9	1009 1 1
£806 Victoria 3% Stock, 1929/49	708 9 0	797 18 9
£4498 11s. 5% Conversion Loan, 1944/64	4367 4 10	5508 19 1
£5164 18s. 9d. 3½% Conversion Stock, 1961, or after	3898 14 10	5733 16 0
	£14,443 2 0	£17,788 12 11

SPECIAL PUBLICATIONS FUND.

Nominal Details.	Value or Cost when Acquired. £ s. d.	Market Value 31st December, 1934. £ s. d.
£2115 3s. 10d. 3½% Conversion Stock, 1961, or after	£1600 0 0	£2348 2 10

SPECIAL LECTURES FUND.

Nominal Details.	Value or Cost when Acquired. £ s. d.	Market Value 31st December, 1934. £ s. d.
£1299 9s. 4d. 3½% Conversion Stock, 1961, or after	£1000 0 0	£1443 8 2

STAFF PENSIONS FUND.

Nominal Details.	Value or Cost when Acquired. £ s. d.	Market Value 31st December, 1934. £ s. d.
£683 6s. 1d. 3½% Conversion Stock, 1961, or after	527 13 0	728 9 4
£371 17s. 1d. 5% Conversion Loan, 1944/64	375 0 0	460 3 4
	£902 13 0	£1218 12 8

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

Nominal Details.	Value or Cost when Acquired. £ s. d.	Market Value 31st December, 1934. £ s. d.
£61 15s. 3d. 3½% Conversion Stock, 1961, or after	50 1 5	68 11 7
£1285 London, Midland and Scottish Railway 4% Debenture Stock	1051 6 6	1361 13 6
	£1101 7 11	£1430 5 1

I have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balances at the Bankers and the Investments. The figures relating to the Bureau of Chemical Abstracts are included in the above accounts subject to the production of certified accounts by the Bureau.

W. B. KEEN,
Chartered Accountants

96, Queen Victoria Street, E.C. 4.
19th February, 1935.

Approved { HENRY J. S. SAND.
H. PAGET.
W. MOORE OCKLEY.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 28th, 1935.

By GILBERT T. MORGAN, O.B.E., D.Sc., LL.D., F.R.S.

Recent Researches on Certain of the Rarer Elements.

FOR the last five years, Presidential Addresses to the Chemical Society have been devoted wholly or in part to considerations affecting the professional and scientific activities of British chemists, and it is undoubtedly the fact that ideas of federation and co-operation have for some time past been stirring in the minds of many members both of this Society and of kindred associations. Discussions have now been in progress for more than two years between representatives of the three Chartered bodies, the Chemical Society, the Institute of Chemistry, and the Society of Chemical Industry. An agreed scheme of co-operation drafted in legal form has now been published and circulated to all members of these three bodies. If this document receives the final approval of the Councils concerned it will mark the first step towards a federal reunion of the institutions representing chemical science in this country.

The Provisional Council, which under the able and zealous Chairmanship of Mr. J. Davidson Pratt has conducted these negotiations, has every confidence that its draft scheme will meet with general approval and if this anticipation is realised it is highly probable that other chemical associations may wish to participate. If such accessions are realised the movement for federation will acquire still greater impetus. As, however, the matter is now before the chemical public, I do not propose to ventilate it further this afternoon but to employ the short time at my disposal in discussing a purely chemical topic.

Organic Derivatives of Selenium and Tellurium.

Fifteen years ago it was known that acetylacetone, the most frequently studied of the β-diketones, furnished with a majority of the chemical elements derivatives which could be classified into three main groups :—

I. Metallic acetylacetones in which the principal valencies of the metal are satisfied completely by a univalent radical $C_5H_7O_2'$. To this group belong the acetylacetones of aluminium, beryllium, chromium, copper, iron, scandium, thorium, zinc, and numerous others.

II. Acetylacetones of the non-metals, metalloids and metals in which the principal valencies of these elements are only partly satisfied by the univalent radical. Such are the compounds of boron, silicon, and titanium, which function as ionised chlorides, giving rise to complex double salts (Dilthey, 1905). To this group also belong certain complex acetylacetones, for instance, those of platinum, $[2C_5H_7O_2' Pt^{II} Cl]M$, where $M = H$, Na, K, or Rb (Werner, 1901), and of cobalt $[C_5H_7O_2' Co, 2en]X_2$, where $X = Cl$, Br, or I (Werner, 1918).

III. Acetylacetones of sulphur which are true organic derivatives of this element containing the non-metal in direct attachment with carbon and not through the intervention of oxygen as in the preceding groups (Angeli and Magnani, Negri, 1893; Vaillant, 1894). Such sulphur derivatives would probably repay further study.

Subsequent researches in the Birmingham University laboratories added gallium to the first group (1921), germanium and zirconium to the second group (1924), and selenium to the third (1922). The late Dr. T. V. Barker, who participated in the last-mentioned research, showed that the selenium derivative was isomorphous with the corresponding sulphur compound.

Acetylacetone Derivatives.

$$C_5H_7O_2' = CH{<}{\begin{array}{l}C(CH_3)\cdot O^-\\C(CH_3){:}O\end{array}}$$

Tl^I·C$_5$H$_7$O$_2$	[B(C$_5$H$_7$O$_2$)$_2$]Cl	S(C$_5$H$_7$O$_2$)$_2$
Be(C$_5$H$_7$O$_2$)$_2$	[Si(C$_5$H$_7$O$_2$)$_3$]Cl	
Al(C$_5$H$_7$O$_2$)$_3$	[Ti(C$_5$H$_7$O$_2$)$_3$]Cl	S$_2$(C$_5$H$_7$O$_2$)$_2$
Sc(C$_5$H$_7$O$_2$)$_3$		S$_3$(C$_5$H$_7$O$_2$)$_2$
Cr(C$_5$H$_7$O$_2$)$_3$	[Ge(C$_5$H$_7$O$_2$)$_2$Cl$_2$]	
Th(C$_5$H$_7$O$_2$)$_4$	[Ge(C$_5$H$_7$O$_2$)$_3$]Cu^{I}Cl$_2$	
	(1924.)	

Ga(C$_5$H$_7$O$_2$)$_3$	[Zr(C$_5$H$_7$O$_2$)$_3$]Cl	Se$_2$(C$_5$H$_7$O$_2$)$_2$
(1921.)	(1924.)	(1922.)
(I.)	(II.)	(III.)
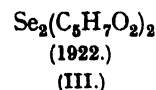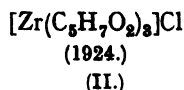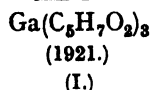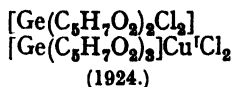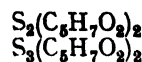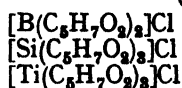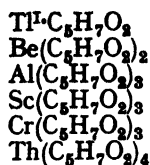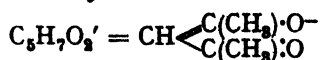
Although the members of these three groups of acetylacetone derivatives differ considerably in type, they possess one attribute in common. They contain the same univalent radical C$_5$H$_7$O$_2'$, of which one or more are present in all the acetylacetone derivatives examined up to 1920.

In that year, Dr. Drew and I began a study of the interactions between acetylacetone and the tetrachlorides of selenium and tellurium. Our preliminary experiments showed that the main products differed from all previously known acetylacetone derivatives in containing a bivalent radical C$_5$H$_6$O$_2''$, and although fourteen years have elapsed selenium and tellurium still remain the only two elements which are known to give this result. I propose in the first place to summarise the advance in chemical knowledge which has accrued from these observations.

Acetylacetone.

Isomeric and Tautomeric Forms.
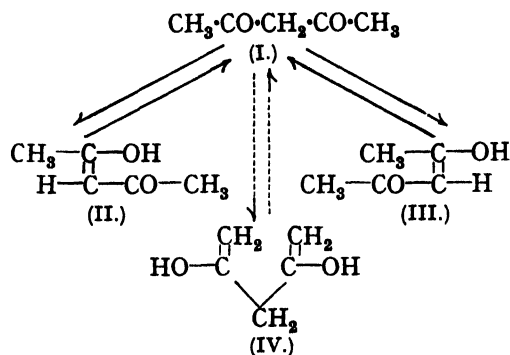
Acetylacetone is commonly known as an equilibrium mixture of the diketone (I) with its monoenolic modification, the latter probably existing in two stereoisomeric forms (II and III). The acetylacetone derivatives known up to 1920 are all derived from the *trans*-monoenolic form of this β-diketone, so that when the hydroxylic hydrogen is replaced by a metal or metalloid the remaining organic residue furnishes a five-membered chelate group which implicates the metallic or metalloidal atom in a six-membered ring.

I now propose to show first that the other *cis*-monoenolic form is operative in the condensations with selenium tetrachloride and secondly that a fourth tautomeric modification is revealed in the condensations with tellurium tetrachloride. It will be obvious that there are several other tautomeric forms of the β-diketone possible between the limits of two-fold terminal enolisation and either of the monoenolic forms. In these intermediate phases, enolisation will be partly terminal and partly median. Evidence

of the intervention of such intermediate forms will also be disclosed in the tellurium tetra-chloride condensations. Actually the experimental demonstration of these new modes of β-diketone interaction was the work of many investigators spread over several years, for at the outset it was supposed that the organic bivalent radical $C_5H_6O_2''$ involved was the same in both cases.

Acetylacetone with Tetrachlorides of Selenium and Tellurium.

(Early interpretation of the selenium and tellurium reactions.)

$$2SeCl_4 + 4C_5H_8O_2 = [C_5H_6O_2\!:\!Se]_2 + 2C_5H_7ClO_2 + 6HCl$$

$$[C_5H_6O_2\!:\!Se]_2 + 4RHSO_3 = 2C_5H_8O_2 + 2Se(SO_3R)_2$$

$$R = H, Li, Na, K, Rb, Cs, [NH_4], or Ba_{\frac{1}{2}}$$

$$TeCl_4 + C_5H_8O_2 = C_5H_6O_2\!:\!TeCl_2 + 2HCl$$

$$C_5H_6O_2\!:\!TeCl_2 + H_2SO_3 + H_2O = C_5H_6O_2\!:\!Te + H_2SO_4 + 2HCl$$
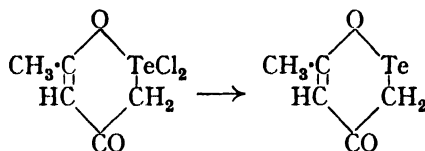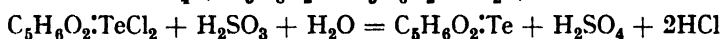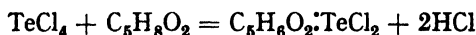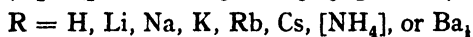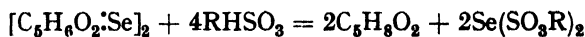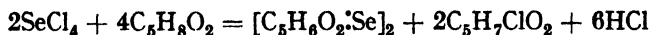
The above scheme indicates the observed condensations. In the reaction with selenium tetrachloride the selenium parted with all its chlorine and yielded a dimeric product containing two molecular proportions of the bivalent radical combined with two atomic proportions of selenium; the other products were 3-chloroacetylacetone and hydrogen chloride.

A practical outcome of this part of the work was soon noticed. This selenium acetyl-acetone was reduced quantitatively by sulphurous acid or aqueous bisulphites. Acetyl-acetone was regenerated and selenodithionic acid or its salts were obtained free from other seleniferous products. These salts were obtained crystalline; the free acid was concentrated to a 50% aqueous solution.

The main reaction with tellurium tetrachloride led to tellurium acetylacetone dichloride, reduced by sulphurous acid or aqueous bisulphite to yellow tellurium acetylacetone.

Our first deductions from these experiments were that in each case we were dealing with the same bivalent radical. Later experiments compelled us to abandon the formulations expressing this view. It will be convenient to take the selenium derivatives first.

Selenium Derivatives of β-Diketones.

The large proportion of hydrogen chloride set free in the selenium tetrachloride reaction exerts a destructive action on the seleniferous product and it was found desirable to diminish this acidity by employing copper acetylacetone rather than the β-diketone itself.

The dimeric selenium acetylacetone (I) contains no enolic group but it reacts with excess of acetylacetone to give rise to selenium *OC*-bisacetylacetone (II), which is mono-enolic as shown by the formation of a copper derivative.

The dimeric compound also reacts with *C*-ethylacetylacetone, hydriodic acid, hydrogen cyanide, and the thionaphthols as shown in the following diagram.

Reactions of Selenium Acetylacetone.

$$CH_3 \cdot C{=\!=}C \cdot CO \cdot CH_3$$
$$\quad OH \quad Se$$
$$\qquad\quad O$$
$$CH_3 \cdot C{=\!=}CH \cdot CO \cdot CH_3$$
(II.)

(I.)
$$\overset{CH_3}{\underset{}{C}}$$
$$CH_3 \cdot CO \cdot C \quad\quad O$$
$$\qquad Se{=\!=}Se$$
$$\qquad O \quad\quad C \cdot CO \cdot CH_3$$
$$\qquad\qquad\quad C$$
$$\qquad\qquad\quad CH_3$$

$$CH_3 \cdot C{=\!=}C \cdot CO \cdot CH_3$$
$$\quad OH \quad Se$$
$$\qquad\quad O$$
$$CH_3 \cdot C{=\!=}C \cdot CO \cdot CH_3$$
$$\qquad\qquad\quad Et$$
(III.)

$2HI$ $C_{10}H_7SH$ (α or β) $2HCN$

(IV.)
$$CH_3 \cdot CO \cdot C{=\!=}C \cdot CH_3$$
$$\quad Se \quad\quad OH$$
$$\quad Se \quad\quad OH$$
$$CH_3 \cdot CO \cdot C{=\!=}C \cdot CH_3$$

(V.)
$$\overset{CH_3}{\underset{}{C}}$$
$$CH_3 \cdot CO \cdot C \quad OH$$
$$\qquad Se$$
$$\qquad S \cdot C_{10}H_7 (α \text{ or } β)$$

(VI)
$$\overset{CH_3}{\underset{}{C}}$$
$$CH_3 \cdot CO \cdot C \quad OH$$
$$\qquad Se$$
$$\qquad CN$$
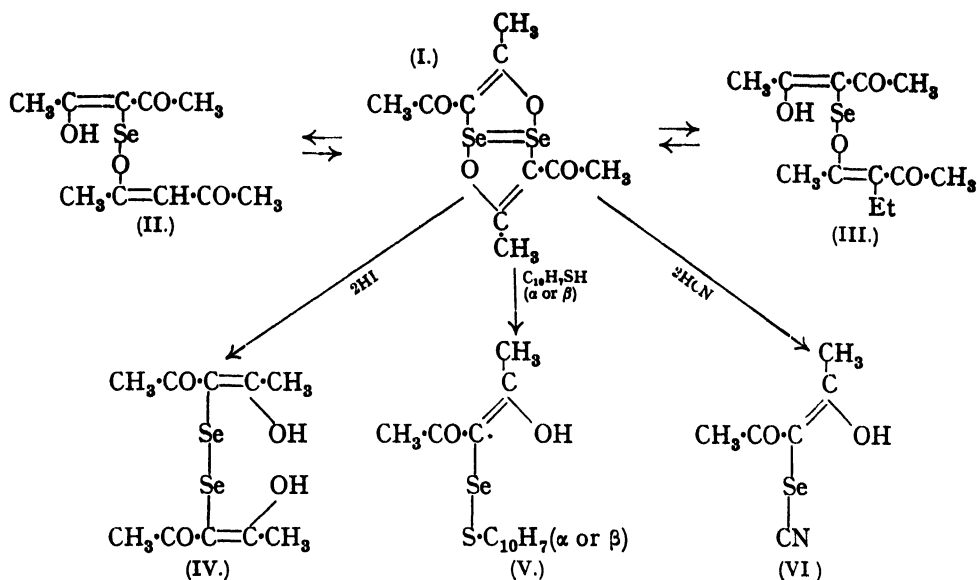
The first reagent gives selenium *C*-ethyl-*OC*-bisacetylacetone (III). The reaction with hydriodic acid goes to completion and the iodine liberated may be estimated quantitatively. The product, diselenium bisacetylacetone (IV), an orange-coloured dienolic compound, may also be prepared by condensing selenium monochloride, Se_2Cl_2, with copper acetylacetone.

With hydrogen cyanide the opening of the ring in selenium acetylacetone proceeds smoothly with formation of a monoenolic selenocyanate (VI), whereas with the thio-naphthols monoenolic thio-ethers (V) are produced.

All these chemical changes support the view that in the dimeric selenium acetylacetone (I), selenium replaces one hydrogen from the enolic radical and one from its attachment to the central carbon atom. The resulting bivalent radical, $C_5H_6O_2''$, is derived from the *cis*-monoenolic form of the β-diketone.

This condensation was extended to other β-diketones such as acetylpropionylmethane, ω-phenylacetylacetone, β-phenylpropionymethane, and benzoylacetone. It was then found that these homologues of acetylacetone, which still contain an unsubstituted methylene residue, all give rise to dimeric selenium derivatives similar in constitution to selenium acetylacetone (I). The condensation with benzoylacetone was noteworthy, since it also led to the compound (VII) which contains three selenium atoms.

The condensations with selenium tetrachloride proceed otherwise when one hydrogen of the methylene group is replaced by an alkyl radical. When the copper derivative of *C*-ethylacetylacetone reacts with selenium tetrachloride, only one hydrogen is displaced from each molecule of the β-diketone. Two products are formed (VIII and IX); they contain respectively one and two atomic proportions of selenium depending on the amount of selenium tetrachloride employed. Both products are non-enolic.

As a final and significant example of these condensations the case of dibenzoylmethane may be cited. The general chemistry of this β-diketone indicates that it enolises somewhat sluggishly. If one of the methylene hydrogens is replaced by halogen, the product is non-enolic. With selenium tetrachloride, two primary products are obtained. One contains two univalent groups attached to one selenium atom (X); the other is a dimeric substance (XI) containing two bivalent radicals, each of which is formed by elimination of two hydrogen atoms originally derived from the methylene group. Hydrogen cyanide reacts with each of these primary products, forming a selenocyanate (XII) which in this case is

non-enolic. Hydriodic acid and the dimeric compound yield a dienolic diselenide (XIII) with liberation of iodine.

Selenium Derivatives of β-Diketones.

(Benzoylacetone, C-ethylacetylacetone, and dibenzoylmethane.)

$$
\begin{array}{ccc}
\underset{\underset{|}{\text{C}}}{\overset{\text{CH}_3}{|}} & \overset{\text{Et}}{\underset{|}{}} & \overset{\text{Et}}{\underset{|}{}} \\
\text{Ph·CO·C} \overset{\text{Se}}{\diagup\diagdown} \text{O} & \text{Me·CO·C·CO·Me} & \text{Me·CO·C·CO·Me} \\
\text{Se——Se} & & \\
\text{O} \quad \text{C·CO·Ph} & \text{Me·CO·C·CO·Me} & \\
\diagdown\!\!/ & \overset{|}{\text{Et}} & \text{Me·CO·C·CO·Me} \\
\underset{\text{CH}_3}{\text{C}} & & \overset{|}{\text{Et}} \\
\text{(VII.)} & \text{(VIII.)} & \text{(IX.)}
\end{array}
$$

Ph·CO·CH·CO·Ph (X.) | Se | Ph·CO·CH·CO·Ph

Ph·CO·CH·CO·Ph | Se | CN (XII.)

(XI.) Ph·C ... Ph·CO·C — O — Se=Se — O — C·CO·Ph ... C·Ph

HCN →   HCN ←

Heat to 145°   Heat   2HI

(XIV.) — Heat to 180° → (XV.)   (XIII.)
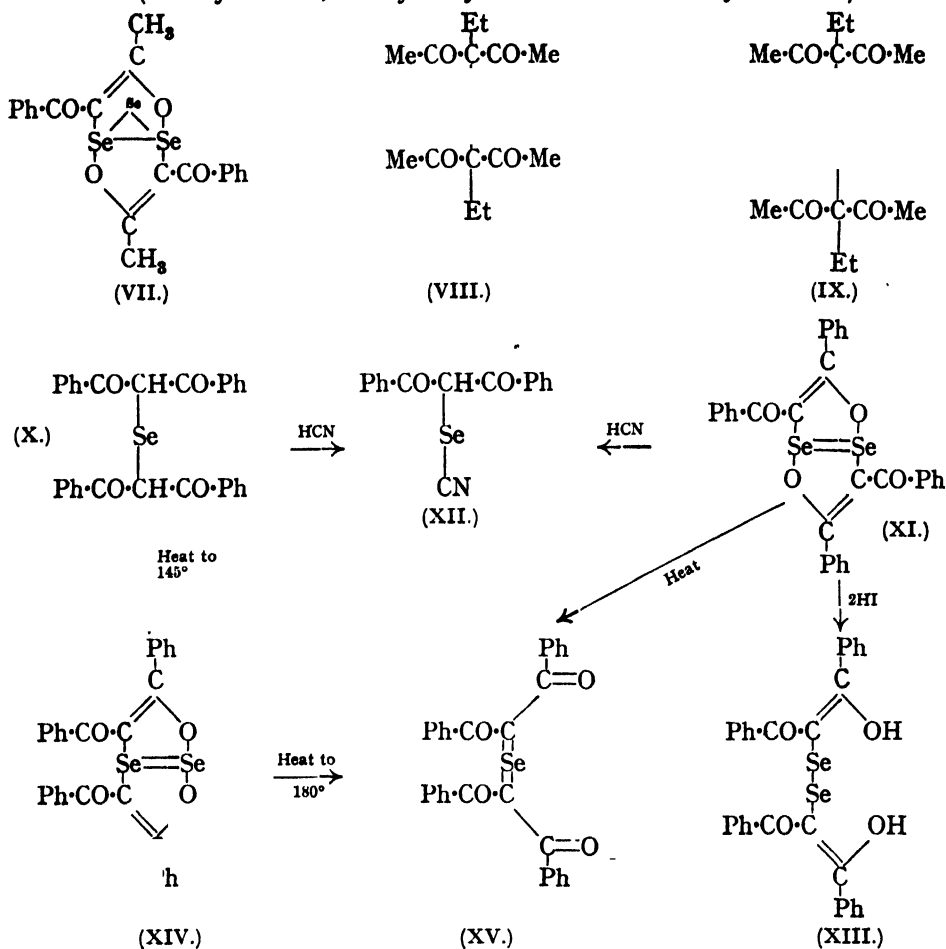
The remaining reactions shown in the diagram were observed only in the case of dibenzoylmethane. On heating gently, the monoselenium compound (X) loses dibenzoylmethane and gives rise to a dimeric substance (XIV) isomeric with the normal one (XI). At higher temperatures this isomeride sheds half its selenium and passes into a compound containing one atomic proportion of selenium associated with two bivalent groups. This orange-coloured dehydrobisbenzoylmethane (XV) is not attacked by hydriodic acid, but when reduced with sodium amalgam in aqueous alcohol it yields dibenzoylmethane, acetophenone, and benzoic acid with elimination of selenium. This reduction throws some light on its constitution.

These experimental results all point to the same conclusion that in reactions between β-diketones or their copper derivatives and selenium tetrachloride the attack of the latter is directed entirely towards the median methylene group so that a bivalent radical is manifested only when, in addition to one enolic hydrogen or its copper equivalent, there is present another hydrogen atom attached directly to the median carbon of the β-diketone. When these two conditions are satisfied, a dicyclic system is established as shown in the revised formulations for all the dimeric selenium derivatives of the series.

Tellurium Derivatives of β-Diketones.

I shall now endeavour to show how in its interactions with β-diketones, tellurium tetrachloride induces a development of the tautomeric forms of these organic reagents. With acetylacetone itself the condensation was effected in ordinary chloroform and under these conditions there were three products. The main product was tellurium acetylacetone dichloride, a compound containing the bivalent radical $C_5H_6O_2''$ combined with a $TeCl_2$ residue. In addition there were two by-products, the first an enolic compound

Non-cyclic Tellurium Derivatives of Mono- and β-Di-ketones containing Univalent Radicals.

I. From Acetylacetone and Homologues

$$\{CH_3 \cdot C(OH) \vcentcolon CH \cdot CO \cdot CH_2\}_2 TeCl_2 \text{ (enolic)}$$
$$CH_3 \cdot C(OC_2H_5) \vcentcolon CH \cdot CO \cdot CH_2 \cdot TeCl_3 \text{ (O-ether)}$$
$$C_6H_{13} \cdot CO \cdot CH \vcentcolon C(OH) \cdot CH_2 \cdot TeCl_3 \text{ or}$$
$$C_6H_{13} \cdot C(OH) \vcentcolon CH \cdot CO \cdot CH_2 \cdot TeCl_3 \text{ (enolic)}$$

II. From Mono-ketones

$$(CH_3 \cdot CO \cdot CH_2)_2 TeCl_2 \qquad C_2H_5 \cdot CO \cdot CH_2 \cdot TeCl_3$$
$$(CH_3)_3 C \cdot CO \cdot CH_2 \cdot TeCl_3 \text{ and } \{(CH_3)_3 C \cdot CO \cdot CH_2\}_2 TeCl_2$$

$$\underset{Cl \text{———} TeCl_3}{R \cdot C(OH) \vcentcolon CHR'} \longrightarrow \underset{Cl \quad TeCl_3}{R \cdot C(OH) \cdot CH_2R'} \longrightarrow R \cdot CO \cdot CHR'TeCl_3$$

$$\underset{R \cdot C(OH) \vcentcolon CHR'}{\overset{R \cdot C(OH) \vcentcolon CHR'}{\underset{Cl}{\overset{Cl}{>}} TeCl_2}} \longrightarrow \underset{R \cdot CCl(OH) \cdot CHR'}{\overset{R \cdot CCl(OH) \cdot CHR'}{\underset{}{TeCl_2}}} \longrightarrow (R \cdot CO \cdot CHR')_2 TeCl_2$$

which retains the property of giving characteristic ferric and cupric derivatives; the second a singular ethyl ether which arises from the circumstance that chloroform B.P. contains ethyl alcohol. These two by-products suggest the intervention of those tautomeric forms of the β-diketone in which enolisation is partly terminal and partly median. With the ascent of the homologous series of β-diketones a fourth type of by-product appears, as in the condensations with dibutyrylmethane, *n*-heptoylacetone and *n*-nonoylacetone. These homologues of acetylacetone furnish tellurium trichlorides of which the product from *n*-heptoylacetone may be formulated as indicated in the above diagram.

At this stage, reference may appropriately be made to a joint study with Mr. O. C. Elvins on the interaction of tellurium tetrachloride and simple ketones. Contrary to the statement of Michaelis's pupil, Rust, acetone does react with the tetrachloride and gives tellurium bisacetone dichloride, $(CH_3 \cdot CO \cdot CH_2)_2 TeCl_2$. The next homologue, methyl ethyl ketone, yields a trichloride, $C_2H_5 \cdot CO \cdot CH_2 \cdot TeCl_3$. Pinacolin (methyl *tert.*-butyl ketone) is of special interest, for it furnishes both types of tellurium derivative, $(CH_3)_3 C \cdot CO \cdot CH_2 \cdot TeCl_3$ and $\{(CH_3)_3 C \cdot CO \cdot CH_2\}_2 TeCl_2$. With increasing substitution of alkyl groups for hydrogen the property of reacting with tellurium tetrachloride gradually disappears. Di*iso*propyl ketone is quite unaffected by this reagent. The two modes of reaction may be generalised as shown in the above diagram.

It is noteworthy that these derivatives of the monoketones containing quadrivalent tellurium are colourless even when R is an aryl group.

One may apply similar reasoning to the interactions of tellurium tetrachloride and β-diketones, of which many examples have been studied. The general formula for any β-diketone which will react with tellurium tetrachloride to form a cyclic compound containing a bivalent chelate group is shown in (I) (following diagram). Under the influence of the tetrachloride the diketone assumes a terminal dienolic form. Addition of the tetrachloride then takes place to give the additive compound (III), separating as an oil from benzene solution, from which hydrogen chloride is eliminated with recovery in the cyclic compound (IV) of the diketo-form.

Cyclic Tellurium Derivatives of β-Diketones.

$$\begin{array}{cc} R\dot{C}H_2 & \dot{C}H_2R'' \\ O\dot:C & C\dot:O \\ & \diagdown C \diagup \\ & R'\diagup \diagdown R' \\ & \text{(I.)} \end{array}$$

TeCl₄

$$\begin{array}{cc} R\cdot\dot{C}H & \dot{C}H\cdot R'' \\ HO\cdot C & C\cdot OH \\ & \diagdown CR_2' \diagup \\ & \text{(II.)} \end{array}$$

→

TeCl₂

$$\begin{array}{cc} R\cdot\dot{C}H & \dot{C}H\cdot R'' \\ Cl\diagdown C & C\diagdown Cl \\ OH\diagup \diagdown\diagup\diagdown OH \\ & CR_2' \\ & \text{(III.)} \end{array}$$

→

TeCl₂

$$\begin{array}{cc} R\cdot\dot{C}H & \dot{C}H\cdot R'' \\ O\dot:C & C\dot:O \\ & \diagdown CR_2' \diagup \\ & \text{(IV.)} \end{array}$$

↓ KHSO₃

Te

$$\begin{array}{cc} R\cdot\dot{C}H & \dot{C}H\cdot R'' \\ HON\dot:C & C\dot:NOH \\ & \diagdown CR_2' \diagup \\ & \text{(VII.)} \end{array}$$

←

Te

$$\begin{array}{cc} R\cdot\dot{C}H & \dot{C}H\cdot R'' \\ HON\dot:C & C\dot:O \\ & \diagdown CR_2' \diagup \\ & \text{(VI.)} \end{array}$$

←

Te

$$\begin{array}{cc} R\cdot\dot{C}H & \dot{C}H\cdot R'' \\ O\dot:C & C\dot:O \\ & \diagdown CR_2' \diagup \\ & \text{(V.)} \end{array}$$

The cyclic dichloride is readily reduced by aqueous alkali bisulphite to give the corresponding *cyclo*telluropentanedione. This is a truly organometalloidal derivative containing bivalent tellurium associated on both sides with carbon and forming part of a heterocyclic six-membered ring. The existence of the two keto-groups in this ring was demonstrated by formation of oximes. Certain of these *cyclo*telluropentanediones yield monoximes (VI), others give dioximes (VII), and some give a mixture of both mono- and di-oximes. This explanation of the mechanism of the formation of the *cyclo*telluropentane ring is supported by the following facts.

1. *Median enolisation.* As long as 2R′ in the general formula (I) represents two hydrogen atoms there is considerable tendency for median enolisation to occur. With acetylacetone it leads to the two non-cyclic products already mentioned. Similar non-cyclic products have also been noticed with propionylacetone, dipropionylmethane, di-*n*-butyrylmethane and heptoylacetone. The last three diketones each exhibited the interesting case of an enolic non-cyclic trichloride (diagram on p. 559).

2. *Alkylation of the median methylene group.* When one R′ is hydrogen and the other an alkyl group, the tellurium tetrachloride condensation becomes simplified so that, although many 3-alkylated β-diketones have been examined, only one telluriferous product has been identified in each case. The case of a branched chain on the median carbon atom is noteworthy. 3-*iso*Propylacetylacetone and 3-*iso*propylpropionylacetone differ from their *n*-propyl isomerides in yielding neither ferric nor cupric derivatives, thus suggesting that an *iso*propyl group may inhibit median enolisation. Nevertheless both these diketones give *cyclo*telluripentanedione dichlorides.

When both R′ are alkyl groups as in the 3 : 3′-dialkylated β-diketones, median enolisation is entirely prevented. Nevertheless 3 : 3-dimethyl- and 3 : 3-diethyl-acetylacetones condense very smoothly with tellurium tetrachloride, giving rise solely to the *cyclo*-telluripentanedione dichlorides. 3-Benzyl- and 3 : 3-dibenzyl-acetylacetones behave similarly and each yields only the one *cyclo*telluripentanedione derivative.

3. *Lengthening of the terminal chain.* So long as the tendency to terminal enolisation is not diminished by alkylation of the terminal methylene group, the lengthening of the hydrocarbon chain R or R″ does not prevent the formation of a *cyclo*telluripentanedione dichloride. This process has been established step by step from acetylacetone to *n*-duodecoylacetone (lauroylacetone).

Both terminal methylene groups must, however, be present. If one is converted into

CHRR', the corresponding β-diketones yield only non-cyclic telluriferous products. The simplest case of a β-diketone with branched chains at both ends was demonstrated with di*iso*butyrylmethane, which was specially prepared for this purpose by Mr. C. J. A. Taylor. In chloroform B.P. this diketone behaved mainly as a reducing agent; nine-tenths of the tellurium present was set free and a very small amount was isolated of a tellurium *O*-ether, $CHMe_2 \cdot C(OEt){:}CH \cdot CO \cdot CMe_2 \cdot TeCl_3$. The influence of aromatic groups is noteworthy. A phenyl group on the median carbon atom as in 3-phenylpropionylacetone inhibits the formation of a tellurium derivative and furnishes an exception to the general rule. A phenyl group at the end of the chain as in benzoylacetone prevents any cyclic condensation; the two products are tellurium bisbenzoylacetone dichloride, $\{Ph \cdot CO \cdot CH{:}C(OH) \cdot CH_2\}_2 TeCl_2$, and the *O*-ethyl derivative, $Ph \cdot CO \cdot CH{:}C(OEt) \cdot CH_2 \cdot TeCl_3$.

I may now sum up the main conclusion of this long series of investigations by saying that the tellurium compounds containing bivalent radicals derived from β-diketones are truly organometalloidal substances containing tellurium implicated in a six-membered heterocyclic ring. The two hydrogen atoms eliminated in producing these bivalent radicals are derived from the enolic groups formed by two-fold terminal enolisation (formula II, p. 560). The primary products contain quadrivalent tellurium and are *cyclo*telluripentane-3 : 5-dione 1 : 1-dichlorides, which are readily reduced by aqueous bisulphites to *cyclo*telluropentane-3 : 5-diones. The latter are yellow substances sparingly soluble in water. In aqueous solution they are powerful germicides and the most potent member of the series, 2 : 6-dimethyl*cyclo*telluropentane-3 : 5-dione, is active against coliform organisms in concentrations of one in 40,000,000. Unfortunately these tellurium compounds are somewhat poisonous and induce hæmaturia. Moreover their bactericidal potency is greatly diminished in serum, probably owing to their adsorption by the small amount of fatty material present in this fluid. These bacteriological and physiological properties have been studied in detail by Dr. E. A. Cooper and several colleagues.

Tellurium Tetrachloride and Acetic Anhydride.

Yellow and colourless forms, m. p. 140—141°.

Ruby-red prisms, m. p. 144°.

Red and black forms.
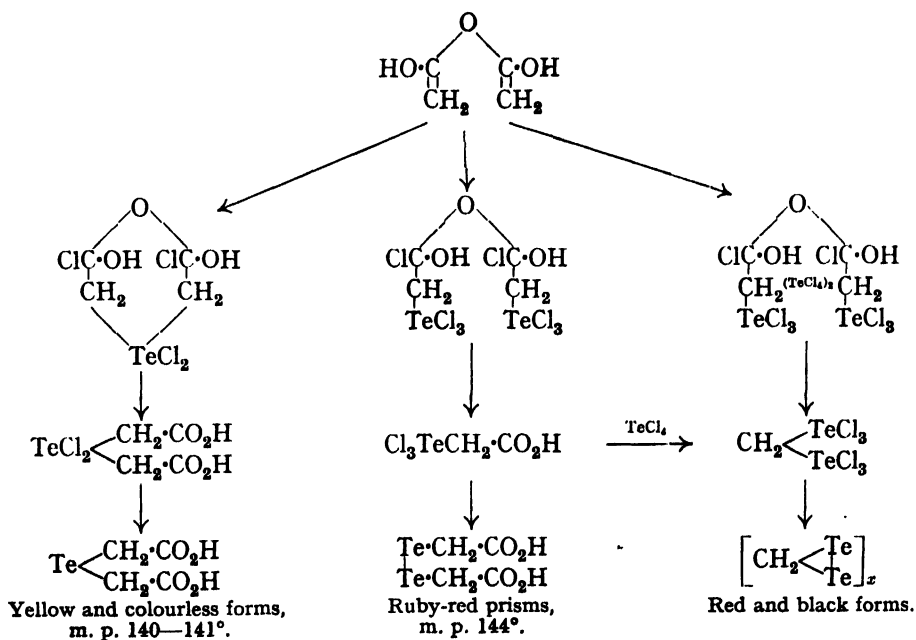
A logical extension of the work on β-diketones led to a study by Dr. Drew and myself of the interactions of tellurium tetrachloride and acetic anhydride. The former research showed that the formation of cyclic compounds was not affected by preventing median enolisation, as, for instance, by two-fold alkylation of the median carbon atom. This

inhibition made no difference, since the attack of tellurium tetrachloride was directed towards the terminal carbon atoms. Accordingly it seemed likely that interaction would persist even if the methylene group were replaced by a single atom such as oxygen. This anticipation was confirmed in a remarkable manner by the condensations occurring between acetic anhydride and tellurium tetrachloride.

The observed chemical changes involved the reaction of acetic anhydride with one, two, or four molecular proportions of tellurium tetrachloride. After hydrolysis, the primary products were respectively dichlorotelluridiacetic acid, trichlorotelluriacetic acid and an oxygen-free methylenebistelluritrichloride. These compounds containing quadrivalent tellurium were reduced by alkali bisulphite and gave rise to tellurodiacetic acid, ditellurodiacetic acid and ditelluromethane. The first compound, a monotellurium derivative, occurs in a colourless and a yellow form. The second and third substances, containing two bivalent tellurium atoms in the molecule, are highly coloured. This association of the group –Te·Te– with a development of colour will appear in another series of tellurium derivatives containing aryl radicals.

Ditelluromethane contains nearly 95% of tellurium, but it is not merely this element contaminated with a little carbonaceous matter. It has definite molecular structure, for by addition of chlorine the hexachloride is regenerated, whereas combination with bromine leads to a yellow hexabromide.

Cyclic Tellurohydrocarbons.

Systematic study of the main products of the interactions of tellurium tetrachloride and the β-diketones has established the existence of ring systems containing one tellurium atom and five carbon atoms. Two of these carbon atoms were oxygenated so that the cyclic compounds were diketones (p. 560).

In collaboration with Mr. F. H. Burstall and with the late Dr. H. Burgess, search was now made for the corresponding *cyclo*tellurohydrocarbons.

The following general methods were devised for the preparation of these cyclic tellurium derivatives : (1) direct combination of finely divided tellurium with alkylene di-iodides; (2) action of alkylene dihalides on aluminium telluride; and (3) interaction in alcoholic medium of alkylene dihalides and sodium telluride.

cycloTelluripropane 1 : 1-*Di-iodide*.—This substance, containing a four-membered ring, was obtained by direct addition of tellurium to trimethylene di-iodide; it is not, however, readily reduced to *cyclo*telluropropane.

I. Small rings.

$$n = 1, 2, \text{ or } 3$$

X = Cl, Br, or I

$$n = 2 \text{ or } 3$$

II. Large Rings.

$$\begin{matrix} \text{IC}_{18}\text{H}_{36}\text{I} \\ \text{IC}_{18}\text{H}_{36}\text{I} \end{matrix} + 2\text{Na}_2\text{Te} = 4\text{NaI} + \text{Te} \begin{matrix} \text{C}_{18}\text{H}_{36} \\ \text{C}_{18}\text{H}_{36} \end{matrix} \text{Te} \qquad (\text{C}_{18}\text{H}_{36}\text{Te})_2$$
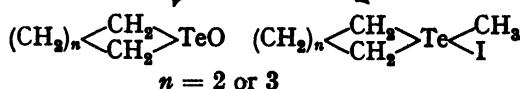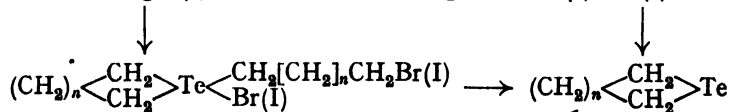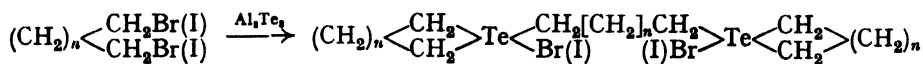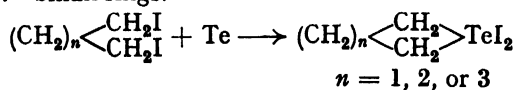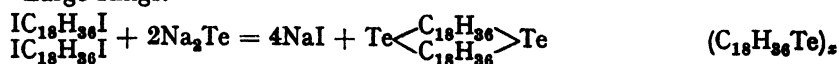
*cyclo*Tellurobutane and *cyclo*Telluropentane.—The five-membered ring system was established through the first general method by heating 1 : 4-tetramethylene di-iodide with tellurium; dark red, crystalline *cyclo*telluributane 1 : 1-di-iodide was then obtained in quantitative yield. Reduction with sulphurous acid led to *cyclo*tellurobutane, obtained as a light yellowish oil with nauseating odour.

The second general method with aluminium telluride was used for both five- and six-membered rings. With this process the *cyclo*tellurohydrocarbon is not isolated in one stage, since it combines additively with more of the alkylene dihalide to yield in each case two complex telluronium salts.

When heated under reduced pressure, these salts dissociate, regenerating the alkylene dihalide and liberating the *cyclo*tellurohydrocarbon, which is converted into its dibromide. This addition product is reduced with alkali metabisulphite to the tellurohydrocarbon, which is extracted with chloroform and distilled subsequently in an inert atmosphere, since it is readily oxidised to a tellurioxide. Its unsaturated character is shown by its combination with methyl iodide.

This study of *cyclo*tellurohydrocarbons indicated that, although the five- and six-membered rings could be prepared with facility, there was but little tendency for the formation of four- or seven-membered rings. As we shall notice later, this preference for five- and six-membered rings is also present among the *cyclo*selenohydrocarbons.

Since, however, the extensive researches of Ruzicka and collaborators during the last ten years have increased our knowledge of large rings with 16 to 30 members, it seemed desirable to ascertain whether it might be possible to include tellurium and also selenium in rings of this order of complexity. The interaction of sodium telluride and 1 : 18-di-iodo-octadecane in alcoholic solution under an inert atmosphere gives rise mainly to a mixture of polymerides of considerable and unknown complexity, but the dimeride $Te_2(C_{18}H_{36})_2$ has also been isolated in a crystalline condition and its molecular weight determined. This product, which resembles its selenium analogue, may contain two tellurium atoms in a 38-membered ring as shown in the above diagram. There was, however, no indication of a *cyclo*tellurohydrocarbon with a nineteen-membered ring.

Cyclic Selenohydrocarbons.

In collaboration with Mr. Burstall, a general method has been devised for the preparation of cyclic selenohydrocarbons, whereby an alkylene dihalide reacts with aqueous alcoholic sodium selenide in an inert atmosphere.

Cyclic Selenohydrocarbons. I.

$$(CH_2)_n{<}^{CH_2Br}_{CH_2Br} + Na_2Se = (CH_2)_n{<}^{CH_2}_{CH_2}{>}Se + 2NaBr$$

$$n = 1, 2, 3, 4, \text{ or } 16$$

I. Small Rings.

$$CH_2{<}^{CH_2}_{CH_2}{>}Se \qquad\qquad CH_2{<}^{CH_2}_{CH_2}{>}SeI_2 \qquad\qquad (C_3H_6Se)_6 \quad (III.)$$
$$(I.) \qquad\qquad\qquad\qquad\qquad (II.) \qquad\qquad\qquad\qquad\qquad \downarrow$$

$$CH_2{:}CH{\cdot}CH_3 + CH_2{<}^{CH_2-Se}_{CH_2-Se}{>} \leftarrow Se{<}^{(CH_2)_3}_{(CH_2)_3}{>}Se$$
$$(V.) \qquad\qquad\qquad\qquad (IV.)$$

$$(CH_2)_n{<}^{CH_2Br(I)}_{CH_2Br(I)} \xrightarrow{KCNSe} (CH_2)_n{<}^{CH_2{\cdot}Se{\cdot}CN}_{CH_2{\cdot}Se{\cdot}CN} \xrightarrow[O]{KOH} {\cdot}(CH_2)_n{<}^{CH_2-Se}_{CH_2-Se} \quad (VII.)$$
$$(VI.) \qquad\qquad\qquad\qquad\qquad\qquad \nwarrow\uparrow_{Br_2}$$

$$(CH_2)_n{<}^{CH_2}_{CH_2}{>}Se{<}^{CH_3}_{I} \leftarrow (CH_2)_n{<}^{CH_2}_{CH_2}{>}Se \rightarrow (CH_2)_n{<}^{CH_2}_{CH_2}{>}SeX_2 \quad (VIII.)$$
$$n = 2 \text{ or } 3 \qquad\qquad\qquad\qquad\qquad\qquad X = Cl, Br, \text{ or } I$$
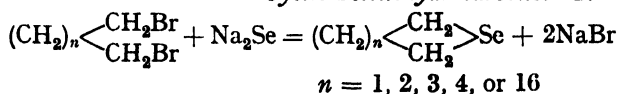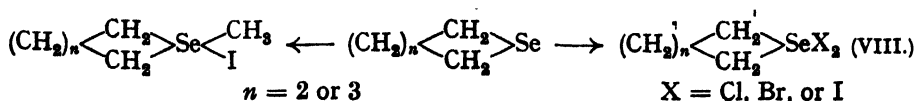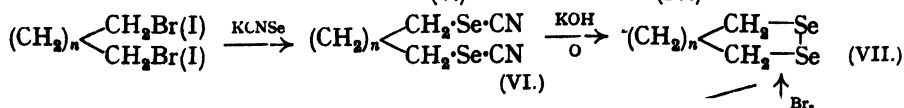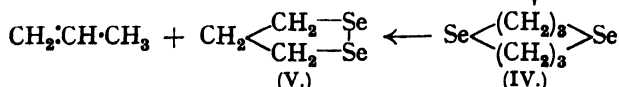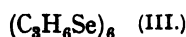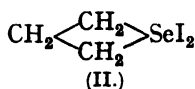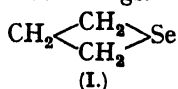
Sodium selenide and 1 : 3-dibromopropane give only a low yield of *cyclo*selenopropane (I) as a readily decomposable liquid of pungent odour. Its di-iodide (II) is a deep purple substance of considerable stability. The main product of this condensation is, however, a six-fold polymeride (III), which on heating is depolymerised to the dimeride (IV). Further pyrolysis leads to *cyclo*-1 : 3-diselenopropane (V) with elimination of propylene.

cyclo*Selenobutane and* cyclo*Selenopentane.*—The two selenohydrocarbons containing five- and six-membered rings are both obtained in excellent yields by the general method. They are stable oils of pungent odour so similar in their chemical properties that the same diagram serves to illustrate their chemical deportment. This diagram indicates an alternative method of preparation based on the interaction of alkylene dihalides and potassium selenocyanate. The organic diselenocyanate (VI) is hydrolysed and oxidised simultaneously to a diselenide (VII), which on heating loses half its selenium and gives the *cyclo*seleno-butane or -pentane. This partial removal of selenium may also be effected by the use of bromine, the dibromide (VIII) being obtained. The comparative instability of the seven-membered ring is indicated in the following diagram.

Cyclic Selenohydrocarbons. *II.*

I. Small Rings.

$$\begin{matrix} CH_2 \cdot CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \cdot CH_2 \end{matrix} \!\!> Se$$
(IX.)

$$(C_6H_{12}Se)_x$$
(X.)

$$Se \!<\! \begin{matrix} (CH_2)_6 \\ (CH_2)_6 \end{matrix} \!\!> Se$$
(XI.)

heat

| heat

$$\begin{matrix} CH_2 \cdot CH_2 \cdot CH_2 \cdot SeCN \\ CH_2 \cdot CH_2 \cdot CH_2 \cdot SeCN \end{matrix}$$
(XIII.)

$\longrightarrow$

$$\begin{matrix} CH_2 \cdot CH_2 \cdot CH_2 \cdot Se \\ CH_2 \cdot CH_2 \cdot CH_2 \cdot Se \end{matrix}$$
(XIV.)

$\longrightarrow$

$$CH_2 \!<\! \begin{matrix} CH_2 \cdot CHMe \\ CH_2 \!-\! CH_2 \end{matrix} \!\!> Se$$
(XII.) | Br$_2$ and heat

$$CH_2 \!<\! \begin{matrix} CH_2 \cdot CHMe \cdot CO_2H \\ CH_2 \!-\! CH_2 \cdot CO_2H \end{matrix}$$
(XV.)

$\longleftarrow$

$$CH_2 \!<\! \begin{matrix} CH_2 \cdot CHMe \cdot CN \\ CH_2 \!-\! CH_2 \cdot CN \end{matrix}$$

$\longleftarrow$

$$CH_2 \!<\! \begin{matrix} CH_2 \cdot CHMeBr \\ CH_2 \!-\! CH_2Br \end{matrix}$$

II. Large Rings.

$$(CH_2)_{16} \!<\! \begin{matrix} CH_2 \\ CH_2 \end{matrix} \!\!> Se$$
(XVI.)

$$Se \!<\! \begin{matrix} (CH_2)_{18} \\ (CH_2)_{18} \end{matrix} \!\!> Se$$
(XVII.)

$$(C_{18}H_{36}Se)_x$$
(XVIII.)

The *cyclo*selenohexane (IX) is a minor product of the general reaction with sodium selenide. The main products are a polymeride of twelve-fold complexity (X), and a dimeride (XI) which probably contains two selenium atoms in a fourteen-membered ring. When these polymerides are heated, they undergo depolymerisation and rearrangement to give rise to 2-methyl*cyclo*selenopentane (XII), a six-membered ring compound which has also been obtained by the diselenocyanate method (XIII) through the eight-membered diselenide (XIV).

The constitution of 2-methyl*cyclo*selenopentane is demonstrated by a series of reactions leading to α-methylpimelic acid (XV), which was identified as its dianilide.

Although these results seem to indicate a limit of stability for the smaller rings at the seven-membered stage, further experiments have been made in order to ascertain whether selenium can be implicated in large rings. Condensation of 1 : 18-dibromo-octadecane and sodium selenide has led to the isolation of a small proportion of monomeric *cyclo*seleno-octadecane (XVI), a nineteen-membered selenohydrocarbon, which is accompanied by a dimeride (XVII), probably containing two atoms of selenium in a 38-membered ring. The latter substance is analogous to a dimeric tellurium compound already described (p. 563). The main condensation product is, however, a polymeride of unknown complexity. The monomeric and dimeric compounds combine with iodine and mercuric chloride, but the addition products are unstable.

Aromatic Derivatives of Selenium and Tellurium.

Selenium Oxychloride and Phenols.—A study with Mr. Burstall of the interactions of the phenols with selenium oxychloride has entailed a revision of earlier work by Michaelis and Kunckel, but a brief reference to the following diagram will indicate the present state of knowledge.

Selenium and Tellurium Derivatives containing Aryl Radicals.

I. $3H \cdot R'' \cdot OH + SeOCl_2 = (HO \cdot R'')_3 SeCl + HCl + H_2O$
with phenol and resorcinol.

II. $3H \cdot R'' \cdot OH + SeOCl_2 = Se(R'' \cdot OH)_2 + Cl \cdot R'' \cdot OH + HCl + H_2O$
with β-naphthol and salicylic acid.
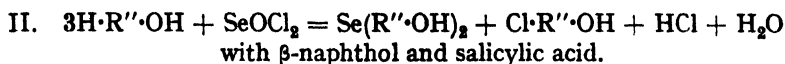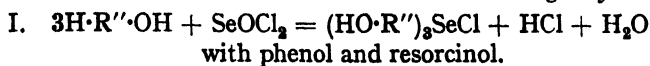
o- and *p-*Cresols give both reactions.
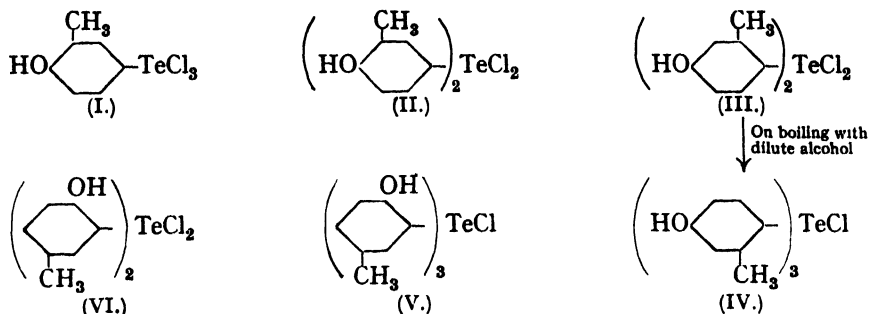
Tellurium Tetrachloride and Anisole or Phenetole

$R = CH_3$ or C_2H_5
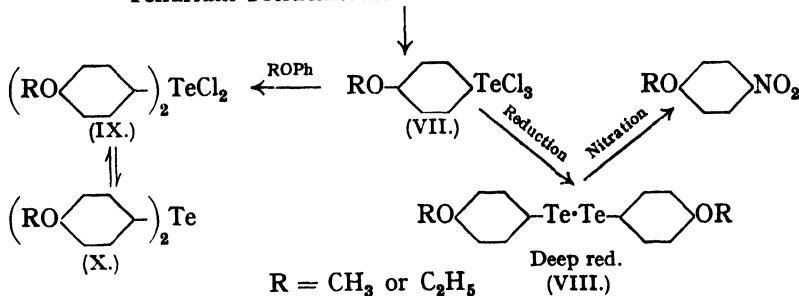
The foregoing workers examined the cases of phenol, β-naphthol and resorcinol and concluded that the two monohydric phenols gave diaryl selenides, $Se(R \cdot OH)_2$, whereas resorcinol was alleged to yield a selenyl derivative $SeO[C_6H_3(OH)_2]_2$. We were able to confirm these statements only in the case of β-naphthol, which furnishes di-2-hydroxydi-1-naphthyl selenide. Salicylic acid gives a similar disalicylyl selenide. Phenol actually gives rise to two trihydroxytriphenylselenonium chlorides, of which the main product is the tri-*p*-substituted compound, and resorcinol yields a similar selenonium chloride. With *o-* and *p-*cresols both types of interaction proceed concurrently, leading to trihydroxytritolylselenonium chlorides and to dihydroxyditolyl selenides.

Basic Tellurium Chloride and Phenols.—With basic tellurium chloride the cresols condense to give products still containing tellurium in combination with chlorine. *o-*Cresol gives a trichloride (I) and a dichloride (II). *p-*Cresol furnishes the polar trihydroxytritolyl-telluronium chloride (V) and the non-polar dichloride (VI). *m-*Cresol yields a non-polar dichloride (III), which on boiling in alcoholic or feebly alkaline solution sheds one third of its tellurium and passes into the polar telluronium chloride (IV).

Tellurium Tetrachloride and Aromatic Ethers.—Tellurium tetrachloride reacts in a characteristic manner with the ethers of phenols and an examination of the products from

anisole, phenetole and similar mixed ethers carried out with Dr. Drew and Mr. R. E. Kellett showed that earlier observations made by Rust and Rohrbaech in the Rostock Laboratories in 1897 and 1901 and those of Lederer made in Ghent during 1915 stand in need of considerable revision. Contrary to the earlier statements the initial product of the condensation with anisole or phenetole is a trichloride (VII) in which an aromatic radical has replaced only one of the chlorine atoms of tellurium tetrachloride. This trichloride when reduced with aqueous bisulphite furnishes the deep red bisaryl ditelluride (VIII). The true dichlorides (IX) were obtained by heating the trichlorides with excess of the corresponding aryl ether. These dichlorides on reduction gave rise to colourless diaryl tellurides (X). Here again one observes the development of colour consequent on the association of two bivalent tellurium atoms in the same molecule. These highly coloured aromatic ditellurides (VIII) may be regarded as analogues of azobenzene.

Extraction of Rare Metals from British Minerals.

Germanium and Gallium from Northumberland Coal Ash. .

In 1933 it was observed by Goldschmidt and Peters that ash from many varieties of coal contains appreciable quantities of the rarer elements and in particular that certain seams in the Northumbrian coal fields gave an ash containing up to 1% of germanium. As this mineral residue appears to be a promising source of rare elements, its investigation has recently been started by Dr. G. R. Davies with the object of extracting from it germanium and any other rare elements which might be present.

In this enquiry, which is still at a preliminary stage, it was found that the germanium content of the ash is extremely variable. The variation may be partly due to irregularities in the occurrence of the germaniferous mineral and partly to loss of germanium during incineration. Being more volatile than the dioxide, the lower oxide, GeO, might be volatilised away unless oxidising conditions prevail in the furnace.

As this Northumbrian ash may also contain up to about 0·05% of gallium, arrangements were made to extract both the rare elements. Germanium is probably present in the coal ash partly as sulphide and partly as oxide. Its extraction is accomplished by a distillation with concentrated hydrochloric acid, germanium tetrachloride passing over accompanied by arsenious chloride and sulphur.

The plant employed is shown in the figure. The still, which has a capacity of 20 litres, has a still-head fitted with stirrer and a delivery pipe leading to a water-cooled worm condenser. Owing to the corrosive nature of the acid, the still, still-head, stirrer, delivery pipe and condenser are all constructed of stoneware. The lower end of the condenser is connected in series with a demijohn of 25 litres capacity, and two wash-bottles, the latter containing aqueous *N*-caustic soda.

About 14 lb. of finely divided ash are introduced into the still with 6 litres of concentrated hydrochloric acid (d 1·16) and an equal volume of 20% acid. This acid mixture is so adjusted that after neutralising the metallic oxides its strength is slightly less than that of the constant-boiling mixture. The still is heated in a gas-fired oil-bath, and the distillation continued for about 30 hours or until a test sample of 150 c.c. gives no precipitate after saturation with hydrogen sulphide. From time to time 20% hydrochloric acid is added in order to replace the loss by distillation. About 10—12 litres of distillate are collected, leaving a residue of 5—6 litres of liquid mixed with a sludge of mineral residue and unburnt coal. The distillate is conveyed to two 10-litre flasks, the liquid from the two wash-bottles added, and the germanium precipitated as white sulphide. After 12 hours' settling, the supernatant liquid is air blown to remove hydrogen sulphide and utilised in subsequent distillations. The moist precipitate of germanium sulphide, which is contaminated with sulphur and arsenious sulphide, is dissolved in 5*N*-sodium hydroxide, and the solution redistilled with hydrochloric acid in a stream of chlorine. Arsenic is thus restored to the quinquevalent condition and rendered much less volatile. The oily germanium tetrachloride in the distillate is either hydrolysed to hydroxide or subjected again to the preceding operations and the purified sulphide hydrolysed to hydrated oxide by boiling with water in a current of carbon dioxide.

Any gallium present in the ash remains in the still as trichloride and is separated from the large excess of iron by ether extraction according to Swift's method (*J. Amer. Chem. Soc.*, 1924). For this separation the iron must be present in the ferrous condition, which is mainly the case, but reduction is completed by zinc or hydrogen sulphide. The still liquor is then extracted with ether for 4 days, a layer of mercury being placed at the base of the extractor to prevent aerial oxidation. In spite of this precaution some ferrous salt is oxidised to ferric chloride, which dissolves in the ether. After removal of ether from the extract the dissolved chlorides are converted into sulphates and these salts are dissolved in a large bulk of water. This solution, almost neutralised with sodium carbonate, is boiled with sodium thiosulphate, neutralisation being completed with aniline (Moser and Brukl, 1929). The crude gallium oxide is redissolved in dilute sulphuric acid and the
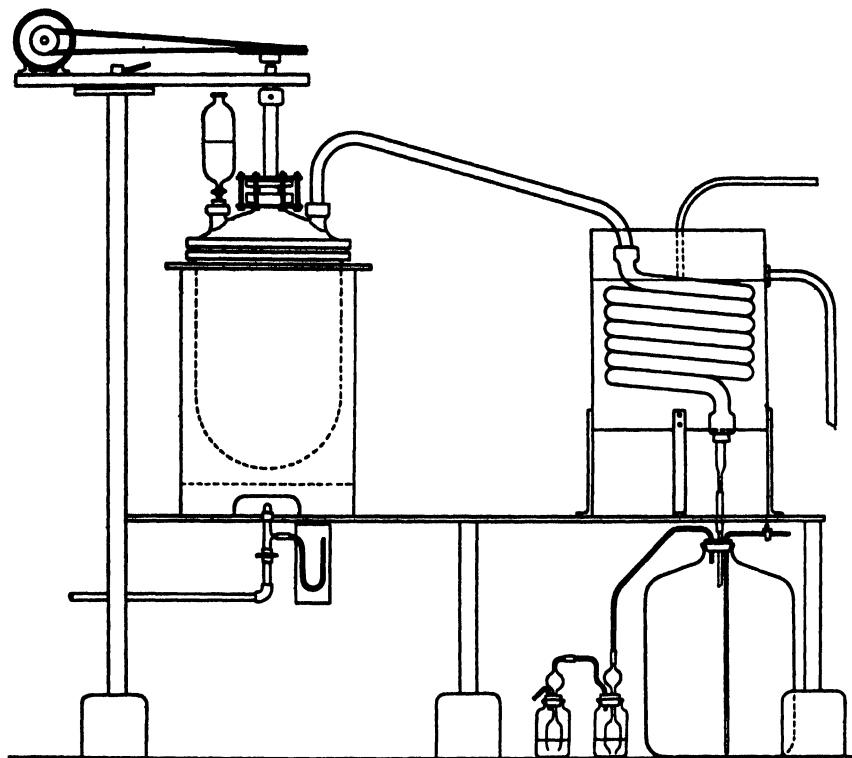
iron present is reduced to the ferrous state. The solution is neutralised partly with sodium carbonate and completely by boiling with cuprous oxide. The precipitate of crude oxide is again dissolved in dilute sulphuric acid, and excess of copper removed with hydrogen sulphide. Addition of ammonia to the concentrated filtrate precipitates gallium hydroxide, which is ignited to gallia.

Rhenium from Australian Molybdenite.

As Australian molybdenite has not previously been tested for rhenium, a detailed examination of this mineral has been made to ascertain whether it could be used as a convenient source of the rare element. This molybdenite in batches of 11—13 lb. was treated with 20—22 litres of nitric acid (*d* 1·4) in a steam-jacketed tantiron pan until 50 lb. of mineral had been used. Oxidation proceeded rapidly with copious evolution of nitrous fumes and sulphur dioxide. The temperature, which rose to 75° or 80°, was maintained by external heat. The resulting greyish-white mass was made up to 90 litres with water, and molybdenum trioxide collected with a porcelain stream-line filter and washed in a filter press. The total filtrate, now amounting to about 85 litres, was con-

centrated in a steam-jacketed enamelled pan. As evaporation proceeded, more trioxide separated and at 22 litres the solution was diluted with its own bulk of water, neutralised with aqueous ammonia (d 0·88), and treated with sodium phosphate and sufficient nitric acid to precipitate yellow ammonium phosphomolybdate, which was collected after 2 days. The filtrate, neutralised with ammonia, was treated successively with ammonium sulphide and dilute sulphuric acid to precipitate mixed sulphides of molybdenum and rhenium, which were dissolved in nitric acid and the solution evaporated with sulphuric acid. This concentrated solution was distilled in hydrogen chloride up to 200°; the distillate when passed into water gave a solution of the hydrated oxides of molybdenum and rhenium. In this distillation molybdenum volatilised much more slowly than rhenium and a repetition of the process led to a considerable separation, which was completed by means of 8-hydroxy-quinoline and nitron. The former reagent precipitated molybdenum, the latter produced sparingly soluble nitron per-rhenate.

Complex Salts of Rhenium.

Until quite recently, complex double cyanides of rhenium were unknown but in 1932 a paper appeared by a Polish chemist Turkiewicz describing a compound of this series as $K_3[ReO(CN)_4 \cdot OH]$, prepared by the action of aqueous potassium cyanide on rhenium dioxide. In our experiments potassium per-rhenate, potassium cyanide and hydrazine hydrate were heated together in aqueous solution, from which alcohol subsequently deposited pale pinkish-yellow crystals of $K_2Na[ReO(CN)_4]$. The presence of sodium was due to the use of commercial cyanide, and further experiments with purified potassium salts gave the tripotassium cyanide $K_3[ReO(CN)_4]$.
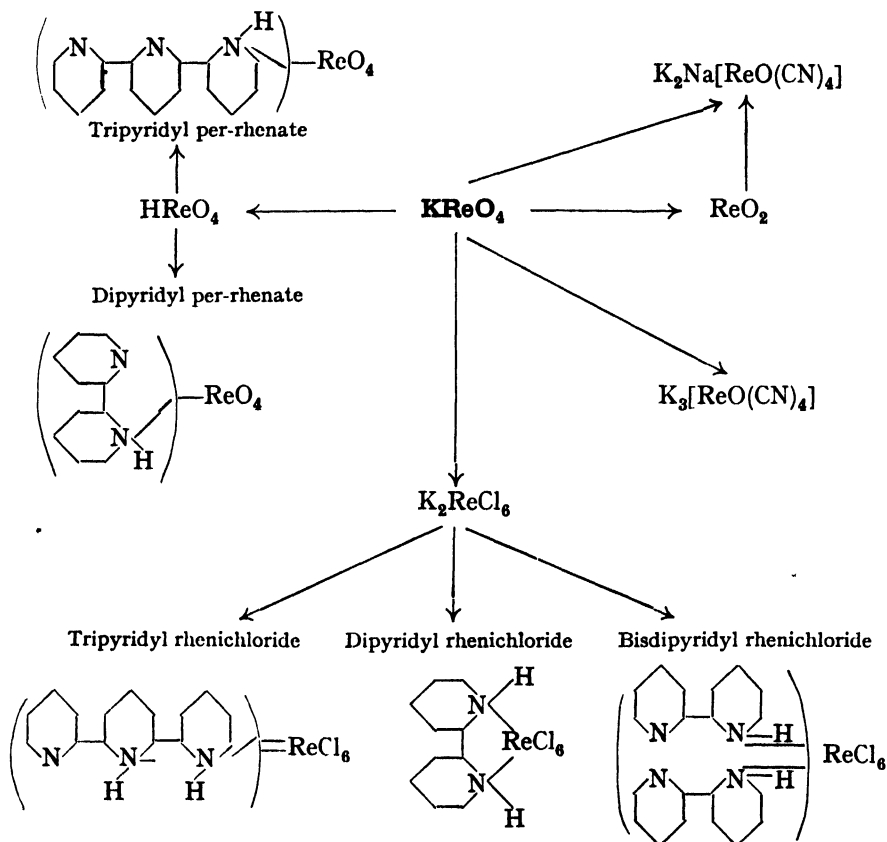
The dipyridyl salts shown in the diagram may serve to separate rhenichloric acid from

per-rhenic acid. 2 : 2′-Dipyridyl rhenichloride, which crystallises in yellow needles, arises from the interaction of its generators in hydrochloric acid. Bis-2 : 2′-dipyridyl rheni-chloride is obtained in pale green, acicular crystals when potassium rhenichloride and 2 : 2′-dipyridyl react in dilute acetic acid. Both salts are sparingly soluble in cold water. 2 : 2′-Dipyridyl per-rhenate is formed on addition of 2 : 2′-dipyridyl in dilute acetic acid to a concentrated aqueous solution of per-rhenic acid. It crystallises in leaf-like clusters of colourless lustrous needles and is more soluble in cold water than the preceding rheni-chloride, since 2·1 grams will dissolve in 100 c.c. of water. 2 : 2′ : 2″-Tripyridyl also gives characteristic salts with the two rhenic acids. With rhenichloric acid it yields only one salt, 2 : 2′ : 2″-tripyridyl rhenichloride, whether the combination is effected in acidic or almost neutral solutions. The colourless product, which dries to a pale green, micro-crystalline powder, is practically insoluble in cold water.

2 : 2′ : 2″-Tripyridyl per-rhenate was prepared from its generators in warm dilute acetic acid as a white crystalline precipitate considerably less soluble in cold water than either the dipyridyl salt or potassium per-rhenate.

During the examination of Australian molybdenite, 2 : 2′-dipyridyl was employed in the final separation of molybdenum and rhenium from a mixture containing 10 parts of Mo to one part of Re. It precipitated 99·5% of the former metal as dipyridyl molybdate, and left in solution 99·6% of the rhenium originally present.

Co-ordinated Ruthenium Compounds.

Early researches on the ammines of ruthenium were made by Claus, the discoverer of this metal (1846), and later these complex salts were studied by Joly (1892 *et seq.*). The latter investigator found that ruthenium trichloride prepared by direct synthesis at 380—400° absorbed ammonia to form $Ru_2Cl_6,7NH_3$, a substance dissolving in water to an intensely red solution. The colouring matter of this liquid, which is known as " ruthenium red," dyes natural silk in red shades. This highly coloured substance is extremely difficult to obtain in a state of purity. The formula $Ru_2(OH)_2Cl_4,7NH_3,3H_2O$ ascribed to it by Joly is scarcely in conformity with modern views on co-ordination.

Ethylenediamine dissolves ruthenium trichloride to form a red solution, but in this case also it is difficult to obtain definite crystalline derivatives. There is no evidence of a similar combination of ruthenium trichloride with 2 : 2′-dipyridyl.

A more promising starting point for the preparation of well-defined co-ordinated ruthenium salts is potassium nitrosoruthenochloride, $K_2[RuNOCl_5]$, an analogue of the well-known potassium nitroprusside,. $K_2[FeNO(CN)_5]$. When this ruthenium salt reacts with 2 : 2′-dipyridyl, two non-ionised compounds are obtained having the structural formula (I). These two isomerides, which are green and reddish-brown respectively, may be obtained·at will by suitably adjusted experimental conditions.

By analogy with the corresponding ethylenediamine compounds (Charonnat, 1931) it is suggested that the red form has the *trans*-configuration (II) and the green form the *cis*-arrangement. Both modifications dissolve in aqueous solutions of such bases as ammonia, ethylenediamine, pyridine, and 2 : 2′-dipyridyl, but the resulting tetrammines are extremely soluble and difficult to isolate.

By employing potassium nitrosoruthenobromide and the corresponding iodide the complex brown tribromide (IV) and black tri-iodide (V) were each obtained but only in one modification. In acid solutions, potassium nitrosoruthenochloride and 2 : 2′-dipyridyl give rise to deep purple crystals of the dipyridyl salt (VI).

A dipyridyl compound of the hydroxo-series is obtained as follows : A solution of 2 : 2′-dipyridyl in dilute hydrochloric acid is added to a solution of the ruthenium chlorides prepared by dissolving hydrated ruthenium oxide in concentrated hydrochloric acid, and chlorine is introduced in order to bring ruthenium to the quadrivalent condition. At this stage the dipyridyl hydroxyruthenichloride (VII) separates in dark brown crystals.

When the tridentate base, 2 : 2′ : 2″-tripyridyl, reacts with potassium nitrosorutheno-chloride, two products are obtained, first a soluble chloride (VIII) crystallising with one

PP

or four molecules of water, and secondly an insoluble complex salt (IX) containing the nitrosoruthenochloride anion.

2 : 2'-Dipyridyl Ruthenium Compounds.
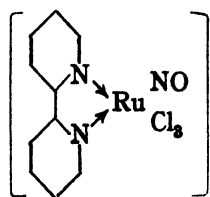
Green and red forms. (I.)	Brown. (IV.)	Black. (V.)
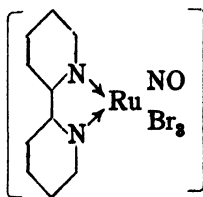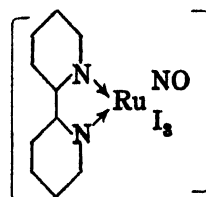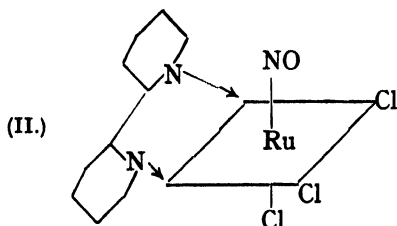
(II.) Red (*trans*).	(III.) Green (*cis*).
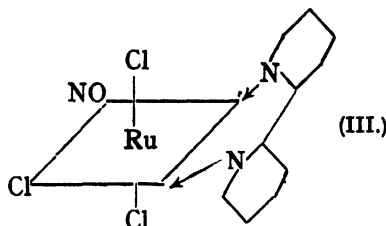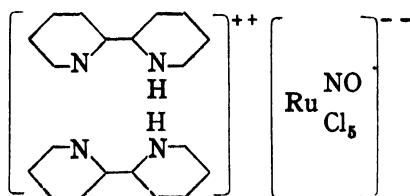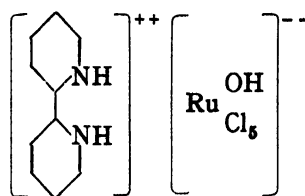
(VI.)	(VII.)

2 : 2' : 2''-Tripyridyl Ruthenium Compounds.

$x = 1$ or 4
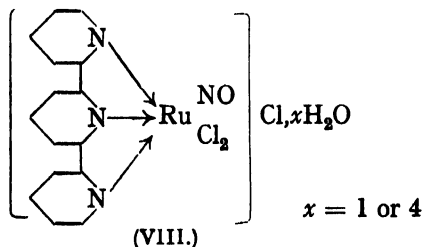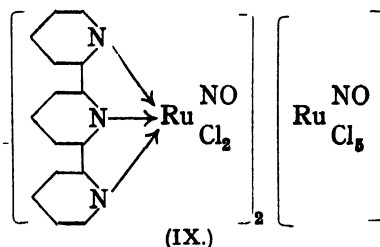
(VIII.)	(IX.)

In pursuing these investigations on ruthenium derivatives we have been greatly assisted by a loan of the metal from the Mond Nickel Company, to whom we desire to express our cordial thanks. The rutheniferous mineral is of British origin, for it was obtained from the Company's mines in Sudbury, Ontario, Canada.

In this Year of Jubilee and national rejoicing I would like to refer to the fact that the British Empire is endowed with mineral resources to an extent unsurpassed by those of any other nation or empire under the sun. These valuable assets involve us in a great responsibility and we ought not to leave the work of exploration entirely to others. A systematic study of the rare elements of the Empire should be a first call on the activities of British chemists. Such researches cannot fail to be of scientific interest and, as in the past, discoveries will from time to time be made in the application of these materials which will redound to the credit of our science and to the good of the community.

125. 1 : 9-*Benzanthrone*-8-*carboxylic Acid and Dibenzanthronedicarboxylic Acid from* 8-*Bromo*-1-*naphthoic Acid.*

By H. Gordon Rule, William Pursell, and (in part) A. John G. Barnett.

The preparation of 8-bromo-1-naphthoic acid in good yield from naphthalic acid (Rule, Pursell, and Brown, J., 1934, 170) has opened up a ready approach to a number of more complex cyclic compounds, which may be obtained by taking advantage of the reactivity of the halogen atom and the carboxyl group. Several new benzanthrone derivatives thus synthesised are described in this and the following communication.

The condensation of methyl 8-bromo-1-naphthoate and methyl o-iodobenzoate with the aid of copper bronze led to the isolation of *methyl* 8-(o-*carbomethoxyphenyl*)-1-*naphthoate* (I), which, on being heated with sulphuric acid, was converted into 1 : 9-*benzanthrone*-8-*carboxylic acid* (II). The acid is orange-yellow, dissolves in sulphuric acid to a deep blood-red solution, and in dilute aqueous alkali yields a yellow solution having a brilliant

(I.)   (II.)   (III.)
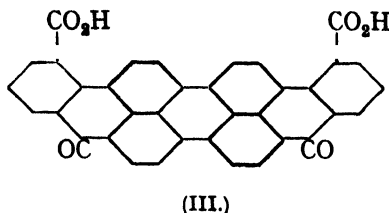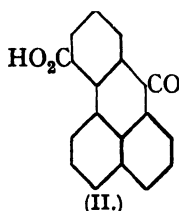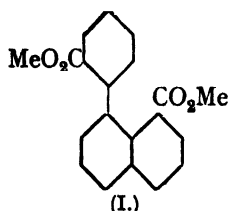
yellowish-green fluorescence. When boiled with quinoline in the presence of copper bronze, it is readily decarboxylated to form benzanthrone.

Dibenzanthrone dicarboxylic acid (III) was obtained in an attempt to convert the very difficultly hydrolysable ester (I) into the corresponding dicarboxylic acid by fusion with alkali : reaction occurred between 265° and 280° to give the deep blue salt of (III) ; above 280°, carbon dioxide was eliminated. The compound is much more readily prepared from benzanthrone-8-carboxylic acid by fusing with alkali at 230°. The dibenzanthrone-dicarboxylic acid is a pure blue vat dye, which is, however, not fast to washing owing to the presence of the free carboxyl groups. Crude violanthrone prepared by the alkali fusion of benzanthrone is a mixture of products, which may be more or less completely separated by taking advantage of their different solubilities in alkali and in acetic acid and their different behaviour towards hydrosulphite (cf. Maki, *J. Soc. Chem. Ind. Japan*, 1932, **35**, 577 B). Such methods were not applicable to the dicarboxy-derivative under discussion, but the product obtained by fusing benzanthronecarboxylic acid with alkali is undoubtedly a mixture, as is indicated by the removal of a more soluble salt on treatment with cold saturated sodium bicarbonate solution, in which the disodium dicarboxylate scarcely dissolves. The purified acid was decarboxylated with quinoline and copper bronze, and the product identified as dibenzanthrone (violanthrone A; cf. Maki) by an examination of the absorption spectrum of a sulphuric acid solution.

Among copper bronzes employed in the Ullmann condensations, the most effective were those exhibiting in bulk a red copper colour ; less active specimens were of a brownish or brassy tint. Gattermann's precipitated copper powder was found even more active than the best copper bronze.

Experimental.

Methyl 8-(o-*carbomethoxyphenyl*)-1-*naphthoate* * was prepared from 25 g. of methyl 8-bromo-1-naphthoate, 38 g. of methyl o-iodobenzoate, and 18 g. of copper bronze, heated for 2 hours in an oil-bath at 215—220°. The product was boiled with 175 c.c. of acetone, and insoluble matter filtered off. Acetone was removed from the filtrate by heating in a vacuum, and the warm syrupy residue treated with 25 c.c. of ether ; crystals were immediately deposited. After 12 hours, these were filtered off and washed with 30 c.c. of ether (yield of mixed esters, 22 g., m. p. 115—127°, consisting almost entirely of phenylnaphthyl and dinaphthyl derivatives).

* Modified preparation by L. A. Bigelow.

From the ethereal mother-liquor, methyl diphenate (5 g.) and the excess of iodo-ester were recovered.

A solution of the mixed esters (22 g.) in 250 c.c. of boiling ligroin was allowed to cool, the clear liquor quickly decanted after 2 hours (longer standing may result in the deposition of methyl dinaphthyldicarboxylate), and the remaining crystals recrystallised from 165 c.c. of ligroin, giving 12·1 g. of methyl 8-(o-carbomethoxyphenyl)-1-naphthoate, m. p. 132—133° (Found : C, 75·2; H, 5·1. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%). A considerable quantity of the ester is retained in the mother-liquors and may be isolated as benzanthronecarboxylic acid by treating the mixed solids with sulphuric acid at 100°.

A small portion of the methyl ester was hydrolysed for 16 hours with concentrated alcoholic potash; 8-(o-*carboxyphenyl*)-1-*naphthoic acid* thus prepared separated from alcohol in colourless plates, m. p. 231—232° (Found : C, 74·0; H, 4·3. $C_{18}H_{12}O_4$ requires C, 74·0; H, 4·1%). The use of less concentrated alcoholic potash for 24 hours gave, in addition to some dicarboxylic acid, a colourless *methyl hydrogen* ester, crystallising from ligroin in compact prisms, m. p. 150—151° (Found : C, 74·4; H, 4·6. $C_{19}H_{14}O_4$ requires C, 74·6; H, 4·3%). When treated in the cold for 30 minutes with sulphuric acid, this compound gave a quantitative yield of benzanthrone-8-carboxylic acid. Hence the unhydrolysed ester group in the ester-acid is that attached to the naphthalene residue, as the isomeric carbomethoxyphenylnaphthoic acid would have been converted into methyl benzanthrone-8-carboxylate under the above treatment (see succeeding paper, p. 573).

1 : 9-*Benzanthrone-8-carboxylic acid*, prepared in almost quantitative yield from methyl 8-(o-carbomethoxyphenyl)-1-naphthoate by heating it for an hour at 100° in sulphuric acid solution, and precipitated by dilution with water, crystallised from alcohol in yellow leaflets, m. p. 273° (Found : C, 78·6; H, 3·8. $C_{18}H_{10}O_3$ requires C, 78·8; H, 3·7%). (For purification of the acid from traces of colouring matter and for its behaviour towards dehydrating agents, see following paper.)

The acid (0·5 g.) was decarboxylated by solution in dry boiling quinoline (5 c.c.), with subsequent addition of copper bronze (0·5 g.). After 20 minutes' boiling, the liquid was filtered, the residue washed with ether, and the mixed filtrates were washed with dilute acid, followed by dilute aqueous alkali. Evaporation of the ether gave crude benzanthrone (0·25 g.), which gave yellow crystalline benzanthrone, m. p. and mixed m. p. 170—171°, on sublimation.

Dibenzanthronedicarboxylic Acid.—Benzanthrone-8-carboxylic acid was fused for 30 minutes at 225—230° with ten times its weight of potassium hydroxide and a few drops of water. The cooled melt dissolved in water to a blue solution, from which a deep blue solid was precipitated on acidification. The crude acid (1·5 g.) was boiled with alcohol, in which it was practically insoluble, and shaken with a cold saturated solution of sodium bicarbonate (50 c.c.), which extracted an impurity forming a brown solution with a brilliant green fluorescence. The bulk of the *dibenzanthronedicarboxylic acid* remained undissolved as the sodium salt, which was filtered off and dissolved in water, and the clear blue solution acidified (yield, 85% of the theoretical) (Found : C, 79·5; H, 2·8. $C_{36}H_{16}O_6$ requires C, 79·4; H, 2·9%).

The compound was readily decarboxylated with quinoline and copper bronze to give dibenzanthrone, as confirmed by appearance and the absorption spectrum of the product in sulphuric acid solution (concn., 1 in 10,000). For the purpose of comparison, commercial violanthrone was separated by the method of Maki (*loc. cit.*) into " violanthrone A " (dibenzanthrone) and " violanthrone B." In sulphuric acid solution the product obtained by decarboxylation transmitted light over the narrow range 5800—6562 Å., as compared with 5950—6680 Å. for dibenzanthrone. Violanthrone B solution transmitted relatively weakly over the wider range 4500—6000 Å. The small observed differences between the first two solutions may conceivably arise from the presence in the dicarboxylic acid of a small amount of an impurity which eventually appears in the final product as " violanthrone B."

126. *The Cyclisation of* 1 : 9-*Benzanthrone-8-carboxylic Acid to* 8 : 11-*Ketobenzanthrone, and of Dibenzanthronedicarboxylic Acid to Diketodibenzanthrone.*

By Lucius A. Bigelow and H. Gordon Rule.

Owing to the indefinite results obtained in a preliminary treatment of benzanthrone-8-carboxylic acid (I) with concentrated sulphuric acid, an extended examination has been made of the behaviour of this compound and its precursor, methyl 8-(*o*-carbomethoxy-phenyl)-1-naphthoate (see previous paper), towards reagents which might be expected to bring about ring closure to 8 : 11-*ketobenzanthrone* (II).

(I.) (II.) (III.)
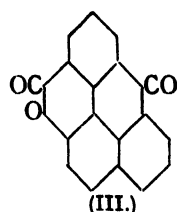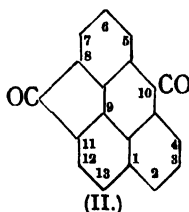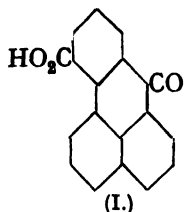
Solutions of the above dimethyl ester in sulphuric acid were maintained for 1 hour at definite temperatures; they were then poured into water, and the products separated. The course of the reaction proved to be unexpectedly complex. The quantities given in the table are those isolated from 1 g. of the dimethyl ester after 1 hour's treatment. Similar results were obtained with methyl benzanthronecarboxylate or the free acid at 130° or higher.

Temp.	Methylbenzanthrone-carboxylate.	Crude benzanthrone.	Benzanthrone-carboxylic acid.	Crude keto-benzanthrone.
16—17°	0·89	—	—	—
50	0·83	—	0·08	—
110	0·13	—	0·74	—
130	—	0·12	0·70	—
150	—	0·19	0·47	0·06
160	—	0·22	0·30	0·13
170	—	0·18	0·16	0·10

Methyl benzanthrone-8-carboxylate was isolated in practically quantitative yield between 15° and 40°. At 50° a little of it underwent hydrolysis, and at 100° benzanthrone-8-carboxylic acid was obtained in 90% yield.

Benzanthrone, produced apparently by decarboxylation of the acid, appeared in small amounts at 120° or higher. The proportion did not increase appreciably with rise in temperature, partly because higher temperatures tended to convert it into a water-soluble sulphonic derivative, which was not isolated, and partly on account of the increasing dehydration of the acid to give ketobenzanthrone (II).

Ketobenzanthrone was formed in small amounts at 135° and upwards, but above 160° disproportionate losses of material occurred by sulphonation. It was always contaminated with a compound, which is provisionally formulated as the *lactone* of 11-*hydroxy-benzanthrone-8-carboxylic acid* (III) and assumed to be formed by oxidation of the acid (the odour of sulphur dioxide is always evident in the sulphuric acid reaction mixture). The lactone may also be prepared in good yield by the oxidation of benzanthrone-8-carboxylic acid with chromic acid. All attempts to confirm the structure by decarboxyl-ation with boiling quinoline and copper bronze, or by methylation to give the methoxy-acid or its ester, failed, the compound being recovered unchanged. Although 1 : 8-naphtholactone also resists decarboxylation by the above method (Rule and Brown, unpublished), no difficulty had been anticipated in methylating the benzanthrone derivative. Nevertheless, this failure is not regarded as excluding the lactone structure, in view of the extremely sparing solubility of the compound and the great tendency of the sodium salt to deposit the neutral product, except in the presence of excess of alkali.

The mixture of lactone and ketobenzanthrone obtained by sulphuric acid treatment

is not easily separated. In organic solvents the lactone is even more difficultly soluble than ketobenzanthrone and it cannot be economically eliminated by recrystallisation. The lactone dissolves in boiling aqueous alkali in a few minutes to give (even a mere trace) an intense purplish-red solution with yellowish-red fluorescence. Ketobenzanthrone, however, also is slowly attacked by hot alkaline solutions, the fluorenone bridge being ruptured with formation of a mixture of benzanthronecarboxylic acids. In spite of the marked disparity in the ease with which the two compounds are attacked, it was not found practicable to purify the crude keto-compound by digestion with hot sodium hydroxide solution, as the separation was always incomplete.

Traces of the supposed lactone are sometimes produced from the ester used as initial material, even when the sulphuric acid treatment is conducted at lower temperatures, as is shown by the purplish-red colour given by the crude benzanthronecarboxylic acid on solution in alkali. By fractional precipitation the lactone, accompanied by a small amount of the acid, may be completely precipitated from such a solution. The purified solution of sodium benzanthrone-8-carboxylate thus obtained on filtration is then orange-yellow and on dilution exhibits a characteristic brilliant yellow-green fluorescence.

Pure 8 : 11-ketobenzanthrone was prepared more simply and in almost theoretical yield by dehydrating the lactone-free carboxylic acid in phthalic anhydride solution at 200° with phosphoric oxide. It was also obtained in small amount by ring closure of the acid chloride by means of aluminium chloride.

The keto-derivative dissolves in concentrated sulphuric acid to a reddish-violet solution having no fluorescence. It gives a deep green solution with dilute alkaline sodium hydrosulphite, the salt of the leuco-compound being sparingly soluble. This solution is readily oxidised in air to deposit the original compound, but the latter is of no value as a dye owing to its instability towards alkalis. This difference from fluorenone, which is not appreciably attacked by aqueous alkalis, probably arises from the greater tension in the 8 : 11-ring in the benzanthrone derivative. In fluorenone the strain in the five-membered ring may be relieved by a slight adjustment of the loose diphenyl system, a distortion which is not so readily tolerated by the more rigid benzanthrone molecule.

Dibenzanthronedicarboxylic acid (see previous paper) exhibited even less tendency than benzanthronecarboxylic acid to undergo ring closure by dehydration when heated with sulphuric acid. In phthalic anhydride solution, however, it reacted with phosphoric oxide to give diketodibenzanthrone, a small amount of the acid being recovered unchanged. The somewhat greater stability of the dibenzanthronedicarboxylic acid towards dehydrating agents is in keeping with the greater rigidity of its molecular structure as compared with that of the corresponding benzanthrone derivative. Diketodibenzanthrone is attacked by boiling aqueous alkalis only with extreme slowness, presumably on account of its insolubility.

EXPERIMENTAL.

The analyses recorded below are micro-determinations carried out by Dr. A. Schoeller, Berlin. All melting points are corrected.

Treatment of Methyl 8-(o-*Carbomethoxyphenyl*)-1-*naphthoate with Sulphuric Acid.*—The ester (1 g.) was dissolved in concentrated sulphuric acid, $d_4^{20°}$ 1·823 (32 c.c. at 16°, or 8 c.c. in other cases), and maintained at the stated temperature ($\pm$ 1°) for 1 hour (see table). The blood-red mixture was then poured into water and the precipitated solids were filtered off and digested for a few minutes with dilute aqueous sodium hydroxide at 60°. The resulting purplish-red suspension was filtered. *Filtrate.* This was treated carefully with sulphuric acid until the first small precipitation discharged the red colour, leaving an orange solution of sodium benzanthronecarboxylate. Precipitated lactone of 11-hydroxybenzanthrone-8-carboxylic acid was filtered off, and the clear liquor acidified with sulphuric acid; it then deposited lactone-free benzanthrone-8-carboxylic acid. *Solids.* These were recrystallised from alcohol, by which means ketobenzanthrone and lactone were readily separated from benzanthrone.

Methyl benzanthrone-8-*carboxylate* crystallised from alcohol in long yellow needles, m. p. 159—160° (Found : C, 79·3; H, 4·2. $C_{19}H_{12}O_3$ requires C, 79·2; H, 4·2%), sparingly soluble in hot alcohol or benzene. In concentrated sulphuric acid it forms a deep orange solution having a yellow fluorescence.

Benzanthrone was obtained as the more readily soluble neutral fraction from sulphuric acid treatment above 120°. After successive recrystallisation from alcohol, ligroin, and benzene it melted at 170—171·5°, and at 170—173° in admixture with a specimen, m. p. 172—173°, prepared from anthranol and glycerol (Found : C, 88·6 ; H, 4·4 ; *M*, in boiling benzene by the Menzies–Wright method, 246, 237, 243. Calc. for $C_{17}H_{10}O$: C, 88·7 ; H, 4·3% ; *M*, 230).

The lactone of 11-*hydroxybenzanthrone*-8-*carboxylic acid* (?). This was first separated in small amount as a very difficultly soluble fraction in an attempt to dissolve in alcohol the carboxylic acid resulting from an experiment at 135°. It crystallised from hot alcohol (0·5 g. dissolves in 450 c.c.), with addition of animal charcoal, in fine golden-yellow needles, m. p. 355—356°.

A solution of benzanthrone-8-carboxylic acid (0·5 g.) in 5 c.c. of concentrated sulphuric acid was poured into 40 c.c. of water, chromium trioxide (2 g.) added, and the mixture heated at 97° with stirring for 4 hours. The pink powder (0·27 g.) obtained by filtration was recrystallised from alcohol, giving the *lactone* (0·16 g.), m. p. 353—355° (softening at 342°), practically unchanged in admixture with the above sample (Found : C, 79·4 ; H, 2·8. $C_{18}H_8O_2$ requires C, 79·4 ; H, 2·9%). About 45% loss of material always occurred during these oxidations, but no anthraquinonecarboxylic acid or other product of oxidation could be isolated.

The compound is not soluble in cold aqueous sodium carbonate ; at higher temperatures it acquires a pink tint without appreciably dissolving. From a benzene solution the lactone can be extracted only extremely slowly by shaking with aqueous caustic soda. In concentrated sulphuric acid it dissolves to a light orange solution showing strong yellow-green fluorescence.

Methylation was attempted, (*a*) by treating the lactone in alkaline solution with methyl sulphate, (*b*) by evaporating the slightly alkaline solution to dryness in a vacuum, removing the remaining water as completely as possible by repeated distillation with toluene, and heating the residual red solid with methyl sulphate, (*c*) with silver oxide and methyl iodide. In all these cases the lactone was largely recovered unchanged.

Cyclisation of Benzanthrone-8-*carboxylic Acid with Phosphoric Oxide.*—The lactone-free acid (4 g.) (see above) was dissolved with stirring in phthalic anhydride (80 g.) at 200°, and phosphoric oxide (4·7 g.) added in two portions at an interval of 30 minutes. After 2 hours the dark red mixture was cooled somewhat and poured into a solution of 50 g. of sodium hydroxide in 450 c.c. of water. The orange precipitate was collected hot, washed liberally with hot water (yield, 3·45 g.), and recrystallised from hot benzene, giving stout orange needles (3·07 g.) of 8 : 11-*ketobenzanthrone*, m. p. 327—328° (softening at 325°, and resolidifying in needles at 323°) (Found : C, 84·2 ; H, 3·2. $C_{18}H_8O_2$ requires C, 84·4 ; H, 3·1%). Both the lactone and keto-benzanthrone have normal molecular weights in boiling benzene.

Diketodibenzanthrone.—Purified dibenzanthronedicarboxylic acid (2·0 g.), dissolved in 100 g. of phthalic anhydride, was heated with stirring for 3 hours at 210°, phosphoric oxide (6 g.) being added in portions during the first 1½ hours. The warm mixture was poured into 450 c.c. of 10% sodium hydroxide solution, and the suspension warmed and filtered. The blue solid was extracted with hot dilute alkali until the filtrate was no longer coloured. It was practically insoluble in boiling quinoline, but dissolved extremely sparingly in boiling nitrobenzene, giving a blue solution with dark red fluorescence. Yield, 1·2 g. The compound formed a purplish-blue vat with alkaline sodium hydrosulphite solution, which dyed cotton a pure blue colour. When the dyed material was boiled for 30 minutes with 1% soap solution, no colour was removed.

127. *Identification of the* 12-*Heteropoly-acids and their Salts by Means of* X-*Ray Powder Photographs.*

By J. W. ILLINGWORTH and J. F. KEGGIN.

THE structures and formulæ of the heteropoly-acids have long been a subject for speculation, and in the literature there is much confusion, in spite of the fact that these acids are important reagents in biological chemistry and in the dye industry. The present work is concerned

with the 12-acids and their salts. Recently, Keggin (*Proc. Roy. Soc.* 1934, *A*, **144**, 75) worked out the structure of 12-phosphotungstic acid, finding the formula of the anion to be $(PW_{12}O_{40})^{-3}$, in agreement with the mass of chemical evidence. Signer and Gros (*Helv. Chim. Acta*, 1934, **17**, 1076), working in these laboratories, later showed that the anions of silico-, boro-, and meta-tungstic acids have a similar structure, their formulæ being, therefore, $(SiW_{12}O_{40})^{-4}$, $(BW_{12}O_{40})^{-5}$, and $(H_2W_{12}O_{40})^{-6}$ respectively. Santos (*Proc. Roy. Soc.*, in the press) has shown that the cæsium salts of these acids contain 3 cæsium atoms in the molecule, with 0, 1, 2, or 3 hydrogen atoms, respectively, in addition.

The exceeding useful *X*-ray powder method has been used throughout these investigations. The structure of the anion was deduced from a powder photograph of the partially dehydrated phosphotungstic acid, for crystals of this hydrate could not be grown in sufficient size for single-crystal work. This was also the case with many of the salts examined. From similarity of diffraction patterns, we deduce similarity of structure. Furthermore, many of the salts of these acids have a structure closely related to that of the acid. The number and position of the metal ions in the molecule of the potassium, rubidium, cæsium, and thallium salts can be deduced from the differences in intensity of certain lines in the diffraction pattern of the salt and that of the acid. In this manner, numerous salts have been prepared and identified : many were new, but we were unable to confirm the formulæ already assigned to several of the known salts.

The analysis of these complex compounds presents many difficulties, and identification by means of powder photographs is much simpler. The exact determination of the number of molecules of water of crystallisation is a matter of some difficulty owing to the high molecular weight, but this can be deduced from a consideration of the space available when the anions are packed together. A further advantage of the method is that one can judge the purity of the substance under investigation by the presence of absence or stray lines. Also, it is a simple matter to test the stability of the compound to, *e.g.*, heat : any decomposition of the anion would be difficult to detect analytically.

Fig. 1 shows a photograph of the pentahydrate of phosphotungstic acid, and Fig. 2 that of the cæsium salt, taken by Santos : the general patterns are the same in both cases. There is, however, a marked difference in the intensities of certain lines (indicated in Figs. 1 and 2), and from these differences Santos was able to show that the molecule of the salt contained three metal atoms. (The spacings of the salt and the acid are slightly different, but the photographs have been suitably enlarged to facilitate comparison.)

The Structure of 12-*Phosphotungstic Acid*. (See Keggin, *loc. cit.*)—The large octahedral crystals grown from aqueous solution of this acid gave a very complicated powder photograph. On dehydration over phosphoric oxide in a vacuum for 2 days, 24 molecules of water of crystallisation were lost, and the weight of the acid became constant. This dehydrated form gave a much simpler diffraction pattern (Fig. 1), and from it Keggin deduced the structure and formula of the anion (see Figs. 4 and 5). The twelve tungsten atoms lie, approximately, on the middle of the edges of a cube, at the centre of which lies the phosphorus atom. Four oxygen atoms form a regular tetrahedron around this phosphorus atom, and the remaining 36 oxygens are so arranged that each tungsten atom is surrounded by an octahedron of six oxygens, as shown for one such atom (W_1) in Fig. 4. The O_1 atom is also shared by the octahedra around W_2 and W_3. There are a number of common edges of the octahedra. The arrangement of the oxygen groups can be seen in Fig. 5, which represents the whole anion.

In the partially dehydrated acid, the packing is cubic, with two molecules per unit cell. The surface of the anion may be considered as consisting of a number of flats (heavily outlined in Fig. 5) and re-entrants. In this packing, the anions are joined flat to flat and re-entrant to re-entrant (see Fig. 6). Of the five molecules of water in this pentahydrate, three are situated at the centres of the faces and the middle of the sides of unit cube, and two between adjoining re-entrants.

Keggin (*Nature*, 1933, **132**, 351) also showed that in the higher hydrate the anions are arranged in a diamond-like packing. There are eight molecules in a unit cell, which has a lattice spacing of 23·28 Å. Recently, Bradley and Illingworth have worked out the position of the molecules of water of crystallisation in this hydrate, and this will be published

$H_3 PW_{12}O_{40}, 5H_2O$

$Cs_3 PW_{12}O_{40}$

FIG 3.

$H_3 PW_{12}O_{40}, 29H_2O$
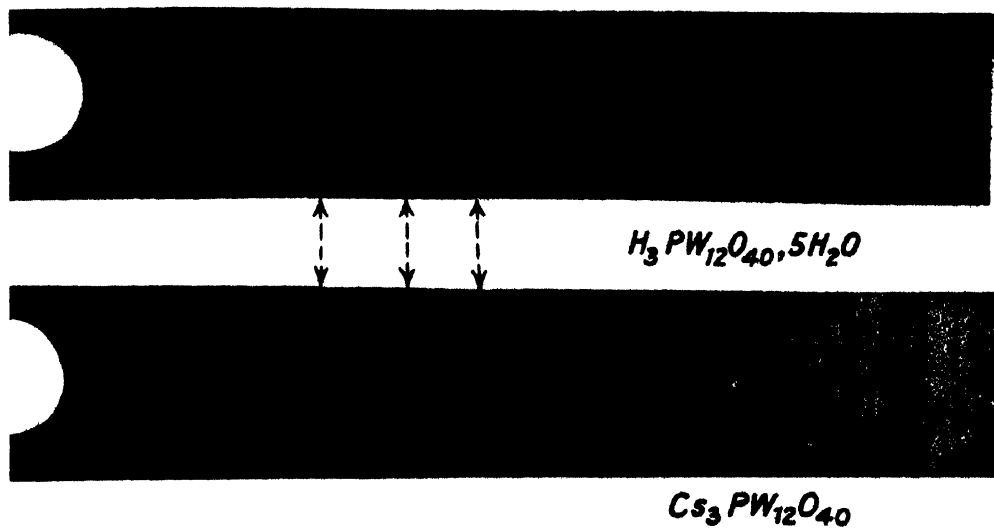
shortly. The anions are joined re-entrant to re-entrant, as shown in Fig. 7. Consideration of this figure shows that there is a large proportion of the cube which is not occupied by the anions, owing to the open nature of the diamond-like arrangement. The water molecules occupy this space, and calculations show that there are 29 H_2O, in agreement with the fact

FIG. 4.
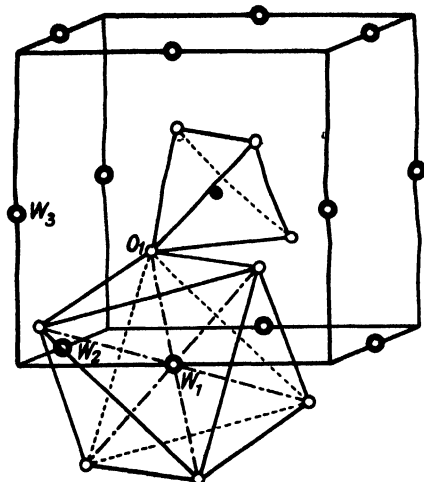
FIG. 5.
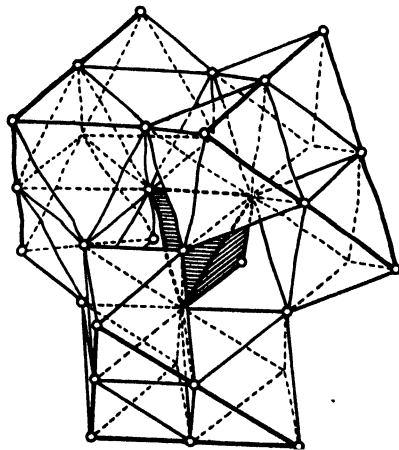
● = *Phosphorus atom.*   ○ = *Oxygen atom.*   ◉ = *Tungsten atom*

that 24 H_2O are lost in the transition from the higher to the lower hydrate. A section of the powder photograph of this hydrate is shown in Fig. 3.*

Santos (*loc. cit.*) found that cæsium phosphotungstate, formed as an insoluble precipitate on addition of a soluble cæsium salt to the acid, without dehydration, gave the packing of

FIG. 6.
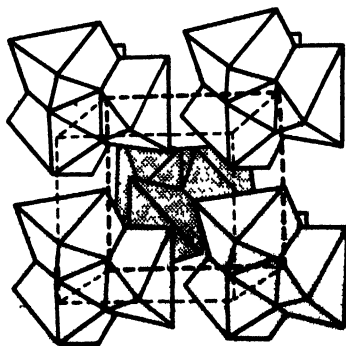
FIG. 7.
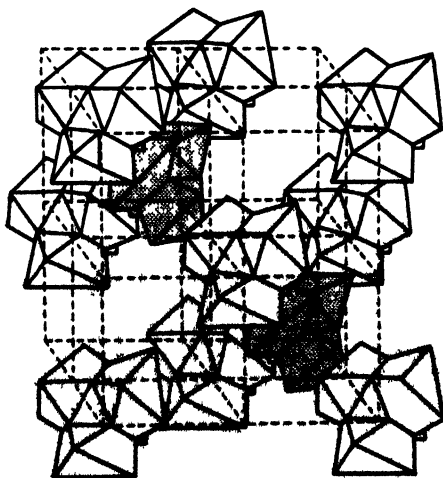
the pentahydrate (Fig. 2). He showed that there are three cæsium atoms per molecule, and they occupy the positions originally filled by the $3H_2O$ at the centres of the faces and the middle of the edges of the unit cube.

The unit cell of those univalent salts which have the pentahydrate packing is smaller

* This photograph was taken in a larger camera than the normal one, and the magnification in Fig. 3 is much greater than in Figs. 1 and 2.

than that of the acid. The size of the anions remains unchanged, but they pack more closely. There is thus less space between the adjoining re-entrants, and in some cases there is not room enough for the molecules of water of crystallisation which occupy this space in the acid state.

EXPERIMENTAL.

The Tribasic 12-Heteropoly-acids and their Univalent Salts.—Phosphotungstic acid. This acid was prepared by Wu's method (*J. Biol. Chem.*, 1920, **43**, 189). It was found that if hydrochloric acid was not added during the last ether extraction, the product was pure 12-phosphotungstic acid, but the omission reduces the yield.

Ammonium phosphotungstate, $(NH_4)_3PW_{12}O_{40}$, is formed as a white, microcrystalline, fairly insoluble precipitate on addition of aqueous ammonium chloride to an acidified solution of the acid.

Sodium phosphotungstate. 50 G. of sodium tungstate dihydrate were dissolved in 100 c.c. of warm water, 5 c.c. of 85% phosphoric acid and 80 c.c. of concentrated hydrochloric acid were added, and the mixture cooled. A white crystalline precipitate of sodium phosphotungstate separated. Its constitution has not been determined, but after being heated for 2 hours at 105° it gave the pentahydrate structure. The formula of this dehydrated form is $Na_3PW_{12}O_{40},nH_2O$, where $n = 2$ or, more probably, 0.

Potassium phosphotungstate, $K_3PW_{12}O_{40}$, is formed as a white microcrystalline powder on addition of a soluble potassium salt to the acid. Unlike the sodium salt, it is fairly insoluble, and no dehydration is necessary to give the pentahydrate structure.

In a similar manner, rubidium, cæsium and thallium phosphotungstates, $M_3PW_{12}O_{40}$, were all precipitated with pentahydrate packing.

Phosphomolybdic acid. This acid was prepared by Wu's method (*loc. cit.*). The yellow octahedra which crystallise from aqueous solution give a powder photograph similar to Fig. 3. The formula is, therefore, $H_3PMo_{12}O_{40},29H_2O$. Attempts to prepare a pentahydrate cubic packing of this acid were unsuccessful. On dehydration, the colour of the acid changed to green, indicating decomposition of the molecule. It is probable that the acid is unstable to the dehydrating conditions necessary to produce the lower hydrate.

On the other hand, the ammonium, sodium, potassium, rubidium, cæsium, and thallium salts all gave the 5-hydrate packing; except the sodium salt, all are very insoluble. The acid will detect 1 part of potassium or cæsium in 10,000 or 500,000 parts of solution, respectively (Illingworth and Santos, *Nature*, 1934, **134**, 971).

Ammonium phosphomolybdate, $(NH_4)_3PMo_{12}O_{40}$, was prepared by adding an aqueous solution of ammonium chloride to an acidified solution of the acid. The canary-yellow precipitate had the usual pentahydrate packing.

Sodium phosphomolybdate is soluble, and can be prepared by addition of sodium chloride solution to the acid. The crystals obtained gave an unknown packing, but on drying for 2 hours at 105°, the normal pentahydrate packing was obtained. The formula of this dehydrated form is $Na_3PMo_{12}O_{40},nH_2O$, where $n = 2$ or 0.

The potassium salt, $K_3PMo_{12}O_{40}$, was similarly prepared; the canary-yellow precipitate showed the usual packing. This compound is very stable, and powder photographs show that its constitution is unchanged after heating for several hours at 120°. The yellow rubidium, cæsium, and thallium salts are prepared in the same manner and have analogous formulæ.

Arsenotungstic acid. No 12-acid is reported in the literature, and all attempts to prepare it were unsuccessful.

Ammonium arsenotungstate is the only salt of the 12-acid previously reported. It is prepared by adding concentrated ammonium chloride solution to a mixture of sodium tungstate and sodium arsenate solutions, strongly acidified with hydrochloric acid. On boiling, a white precipitate, $(NH_4)_3AsW_{12}O_{40}$, is formed. Powder photographs show the normal 5-hydrate packing.

A similar procedure afforded the potassium and the rubidium salt, $M_3AsW_{12}O_{40}$, which are insoluble and have the usual 5-hydrate structure. Attempts to prepare a cæsium salt with a similar packing were unsuccessful.

Arsenomolybdic acid. Here again, no 12-acid is reported, and it could not be prepared.

The ammonium salt, $(NH_4)_3AsMo_{12}O_{40}$, is formed as a canary-yellow precipitate on boiling a mixture of sodium arsenate, sodium molybdate, nitric acid, and ammonium chloride; it has the normal 5-hydrate packing.

The potassium and the rubidium salt were prepared by adding the corresponding chloride to

a boiling mixture of sodium arsenate and sodium molybdate solutions and hydrochloric acid. The canary-yellow precipitates, of formula $M_3AsMo_{12}O_{40}$, are very insoluble.

The Tetrabasic Acids.—Silicomolybdic acid was prepared in a similar manner to the corresponding phosphomolybdic acid, sodium silicate solution being used instead of phosphoric acid. In this case, the ether extraction of the acid is more difficult, and care must be taken to avoid excess of hydrochloric acid, otherwise the ether compound will not form. On standing, the aqueous solution becomes yellowish-green, and hexagonal crystals are formed; these were of unknown packing. If, however, a few drops of nitric acid were added to the acid solution, and crystallisation was effected above 30°, small yellow octahedral crystals were formed. These gave a powder photograph similar to Fig. 3, and their formula is, therefore, $H_4SiMo_{12}O_{40},29H_2O$.

Attempts to prepare the 5-hydrate packing were unsuccessful. The acid, on dehydration, rapidly became green—an indication that the anion was disintegrating.

Ammonium silicomolybdate. Parmentier (*Compt. rend.*, 1887, **92**, 1234) reported the precipitation of a salt, $(NH_4)_4H_4Si(Mo_2O_7)_6,nH_2O$, on mixing nitric acid solutions of ammonium molybdate and alkali silicate. If we assume that the basicity of the acid is not eight but four, then, according to Parmentier, this is a normal salt.

The authors prepared the salt by adding excess ammonium chloride solution to the acid; the canary-yellow precipitate had the 5-hydrate packing. Owing to the comparatively low scattering power of the ammonium ion, it is impossible to deduce from the powder photograph the number of these ions in the molecule. However, symmetry conditions of the structure do not allow of a four position in the 5-hydrate packing, and we concluded that this must be an acid salt, as in the case of cæsium silicotungstate (Santos). Subsequently, chemical analysis proved conclusively that the ammonium content was 3 and not 4; the formula is, therefore, $(NH_4)_3HSiMo_{12}O_{40}$. Attempts to prepare the normal salt were unsuccessful.

The potassium salt was prepared by adding excess potassium chloride solution to the acid; unlike the corresponding phosphomolybdate, it is soluble. If the solution is allowed to crystallise, yellow hexagonal prisms are obtained. These gave an unknown packing, but on heating for 2 hrs. at 120°, the normal cubic packing was obtained. The formula of this dehydrated form is $K_3HSiMo_{12}O_{40}$.

Analogous formulæ are possessed by the rubidium, cæsium, and thallous salts, prepared by adding a solution of a salt of the appropriate metal to the acid; they are all insoluble and give the usual 5-hydrate packing.

Silicotungstic acid. Signer and Gros (*loc. cit.*) showed that the dehydrated form of this acid gave a similar packing to that of phosphotungstic acid, and the formula was therefore $H_4SiW_{12}O_{40},5H_2O$. The higher hydrate, however, was not cubic but hexagonal, and had a similar packing to the hexagonal form of silicomolybdic acid; it lost $24H_2O$ on transition to the 5-hydrate, and is therefore $H_4SiW_{12}O_{40},29H_2O$.

The potassium salt, prepared by adding excess potassium chloride solution to the acid, is soluble. According to various workers, it is the normal salt, but on dehydration it did not give the normal 5-hydrate packing. It is significant that, if the 4-salt is formed, then the packing is no longer that of the 5-hydrate. This is, of course, in agreement with theory.

The thallous salt, $Tl_3HSiW_{12}O_{40}$, is formed as a white precipitate on addition of a solution of a soluble thallous salt to the acid.

The 12-Manganimolybdates.—These salts have not hitherto been described. Attempts to prepare the free acid were unsuccessful.

Ammonium manganimolybdate. 5 G. of sodium molybdate were dissolved in 10 c.c. of water, and 0·5 g. of sodium permanganate added. The mixture was heated, 10 c.c. of hydrochloric acid added, and boiling on the water-bath continued for an hour, the solution becoming deep yellow. The mixture was filtered and excess of concentrated ammonium chloride solution added to the filtrate. On boiling, a pale yellow precipitate formed, having the normal 5-hydrate packing. This salt is derived from the acid $H_nMnMo_{12}O_{40}$, and since manganese may be either quadri- or septa-valent, $n = 4$ or 1. The value of n would be very difficult to obtain by ordinary chemical analysis and no attempt has yet been made to do so. All attempts to prepare a 12-heteropoly-acid with a charge of $+6$ at the centre have been unsuccessful, and we are led to assume that such a charge would render the whole anion unstable. If so, then it appears improbable that a charge of $+7$ can be placed in the centre, and $n = 4$; in agreement with this, the salt has a spacing identical with that of ammonium silicomolybdate (11·63 Å). Analysis indicated 3 ammonium ions per molecule. The formula is, therefore, $(NH_4)_3HMnMo_{12}O_{40}$.

The cæsium salt was similarly prepared by use of cæsium sulphate; the pale yellow precipitate had the 5-hydrate packing.

Germanitungstic Acid.—We are indebted to Mr. W. O'Leary, of Cornell University, for kindly sending us a sample of this acid. Its preparation is described by Brukl (*Monatsh.*, 1930, **59**, 179) and Schwartz and Giese (*Ber.*, 1930, **63**, 2428). No cubic form of the 29-hydrate could be obtained, but after dehydration over phosphoric oxide in a vacuum for 4 days, the weight became constant and the normal 5-hydrate packing was obtained. The formula is thus $H_4GeW_{12}O_{40},5H_2O$.

The white cæsium salt, $Cs_2HGeW_{12}O_{40}$, is precipitated on addition of a soluble cæsium salt to a solution of the acid.

Ammonium Titanimolybdate, $(NH_4)_3HTiMo_{12}O_{40}$.—0·3 G. of titania was fused with excess of acid potassium fluoride on a carbon block, and the resulting white mass added to a solution of 5 g. of sodium molybdate in 10 c.c. of water; 15 c.c. of concentrated hydrochloric acid and a few drops of nitric acid were added, and the whole heated on the water-bath for an hour. The mixture was then filtered, and the filtrate treated with excess of concentrated ammonium chloride solution and boiled; the golden-yellow precipitate had the simple cubic 5-hydrate structure. Great care must be taken in this preparation to avoid contamination with silica, for ammonium silicomolybdate is then formed.

Ammonium zirconimolybdate is prepared in an analogous manner and gives an identical powder photograph.

Borotungstic Acid.—Signer and Gros (*loc. cit.*) showed that this acid has a structure similar to that of $H_3PW_{12}O_{40}$. No cubic form of the 29-hydrate could be grown, but on dehydration of this higher hydrate over phosphoric oxide in a vacuum for 8 days, $H_5BW_{12}O_{40},5H_2O$ was obtained.

Metatungstic Acid.—This belongs to the series of 12-acids. No cubic form of the higher hydrate could be obtained, but dehydration as above for 4 hours afforded $H_6(H_2W_{12}O_{40}),5H_2O$.

The cæsium and the thallous salt, $M_8H_8(H_2W_{12}O_{40})$, are precipitated on addition of a soluble salt of the metal to the acid; the former is fairly soluble in hot water.

Attempts to prepare 12-Acids.—Although metatungstic acid is a 12-heteropoly-acid, all attempts to prepare an analogous metamolybdic acid or its salts failed. No 12-boromolybdates are known, and they could not be prepared. As metamolybdic and 12-boromolybdic acids probably do not exist, we infer that a charge of + 5 or + 6 at the centre of the anion renders the latter unstable in the case of the complex 12-molybdic acids. In the corresponding tungstic acids, the stability of the anion diminishes with increasing charge.

Attempts to prepare 12-stanni-, chromo-, antimono-, and vanado-molybdates were all unsuccessful. Although efforts were made with many elements (*e.g.*, Al and Cr), it was found possible to place only molybdenum and tungsten in the outer shell of the 12-acid.

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128. *Complex Formation between Polynitro-Compounds and Aromatic Hydrocarbons. Part I. Finite Reaction Rates.*

By DALZIEL LL. HAMMICK and GODFREY SIXSMITH.

THE existence in the solid state of well-defined complexes of aromatic polynitro-compounds with aromatic hydrocarbons in simple stoicheiometric proportions has long been recognised. That interaction of some kind may occur between the components in the liquid state is indicated by the colour change that frequently follows their admixture in solution. Further evidence for interaction comes from cryoscopic experiments by the addition to solvents of the components separately and together, the depression in the latter case being less than the sum of the depressions in the former (Behrend, *Z. physikal. Chem.*, 1894, **15**, 183; Brown, J., 1925, **127**, 345). Again, the partition of picric acid between water and an immiscible second solvent is influenced by aromatic hydrocarbons and their derivatives in the latter in such a way that interaction between the picric acid and the hydrocarbon in the non-aqueous layer must be inferred (Bamberger and Dimroth, *Annalen*, 1924, **438**, 67; Moore, Shepherd, and Goodall, J., 1931, 1447). It is not possible, however,

to conclude with certainty from these and analogous results (cf. Baker and Bennett, *Ann. Reports*, 1931, **28**, 137, for bibliography) that the interaction which undoubtedly occurs in the liquid phase is of the nature of true chemical combination, involving the rearrangement of co-ordinate linkages. The nitro-group is highly polar, and aromatic hydrocarbons are polarisable. It may, therefore, well be that equilibrium constants derived from the alterations in the solubility or miscibility of a polar solute caused by the addition of a polarisable second component have no more real significance than the apparent dissociation constants of strong electrolytes calculated from the depressions they cause in the freezing point of water.

As was pointed out by Bamberger and Dimroth (*loc. cit.*), there is one reliable criterion that can be applied to distinguish between polar interaction, resulting possibly in the formation of "dipole aggregates," and true chemical interaction. In the first case, re-action will be analogous to ionic interaction and be practically instantaneous. Chemical interaction, on the other hand, involves activation of the reacting molecules, and in suitable circumstances may be expected to take place at measurable rates. If, therefore, cases can be found of polynitro-compounds reacting slowly with hydrocarbons, the conclusion can be drawn with certainty that ordinary valency forces are involved in the formation of the complexes. We have found one such case in the system methyl 4 : 6 : 4' : 6'-tetra-nitrodiphenate–indene, for we find that a *complex* can be both formed and decomposed at finite rates. We were led to seek for suitable polynitro-compounds among the deriv-atives of diphenyl by the observations of Lesslie and Turner (J., 1930, 1758) and others that such compounds form unusually stable solid complexes with benzene and similar hydrocarbons. Indene was chosen as the second component because it can be estimated rapidly and accurately by means of bromine.

<div align="center">EXPERIMENTAL.</div>

The rates of formation and of dissociation of the specified complex have been studied in carbon tetrachloride solution at 38°, this temperature being necessary in order to obtain sufficiently concentrated solutions of the sparingly soluble ester.

Preparation of Materials.—Methyl 4 : 6 : 4' : 6'-tetranitrodiphenate was prepared by Ullmann and Engi's method (*Annalen*, 1909, **366**, 79), m. p. 176·1° (corr.). The indene used was distilled three times before each experiment (b. p. 182°); a sample prepared in this way and distilled directly into a tared standard flask containing carbon tetrachloride can be pre-served for weeks at concentrations up to $M/10$ without its titre against a standard solution of bromine in carbon tetrachloride changing appreciably. The bromine was purified by Cohen's method (*J. Amer. Chem. Soc.*, 1930, **52**, 2827).

The *compound* of indene with the nitro-ester was prepared by crystallising 1 mol. of ester in the presence of 4 mols. of indene from methyl alcohol; m. p. 159° (corr.) (Found : C, 48·9; H, 2·9. $2C_{16}H_{10}O_{12}N_4,C_9H_8$ requires C, 48·6; H, 2·8%. 0·0173 G. reduced 13·1 c.c. of 0·0617N-TiCl$_3$. Calc. : 13·1 c.c.) : it is decomposed into its constituents on recrystallisation from methyl alcohol in the absence of excess indene.

Estimation of Indene.[*]—We find that indene in dilute solution ($M/10$ or less) can be estimated accurately by adding an excess of bromine in carbon tetrachloride, the unreacted bromine being immediately removed by shaking with an aqueous solution of potassium iodide. The liberated iodine is titrated with standard thiosulphate. Under these conditions exactly 2 atoms of bromine react with 1 mol. of indene.

The carbon tetrachloride used as solvent was free from sulphur and free chlorine, and was distilled from phosphoric oxide before use.

Decomposition of the Compound in Solution.—Weighed quantities of the compound were dissolved as rapidly as possible in carbon tetrachloride at the temperature of the thermostat and made up to 50 c.c., either with pure solvent or with a solution of indene in carbon tetra-chloride. Aliquot parts were removed at successive intervals of time, and the free indene estimated as described above. The following results were obtained at 38° for the rates of decomposition of the compound alone (Expts. I and II) and in the presence of free indene (Expts. III and IV). 5-C.c. portions of the solution of compound were treated with 5 c.c. of

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[*] The conditions under which indene can be preserved and estimated have been worked out and will be described in a later communication.

0·054N-bromine in carbon tetrachloride in Expt. I, and with 10 c.c. of 0·0445N-bromine in carbon tetrachloride in Expts. II, III, and IV. In all cases the unreacted bromine was estimated in terms of $N/100$-thiosulphate. In the tabulated results, C_0 is the initial concentration of the compound, and all concentrations are expressed as g.-mols. per 1000 litres.

Experiment I. $C_0 = 9·614.$

t (mins.)	5	10	20	29·5	40	78	121	1095
C.c. $N/100$-Na$_2$S$_2$O$_3$	24·4	23·0	22·3	21·4	20·3	20·0	20·0	20·0
Indene	2·6	4·0	4·7	5·6	6·7	7·0	7·0	7·0

Experiment II. $C_0 = 9·444.$

t (mins.)	4	10	16	19	39	64	107	1008
C.c. $N/100$-Na$_2$S$_2$O$_3$	43·0	41·5	40·1	39·65	38·1	37·6	37·5	37·6
Indene	1·5	3·0	4·4	4·85	6·4	6·9	7·0	6·9

Experiment III. $C_0 = 22·550$; C_0 indene $= 11·50.$

t (mins.)	2	5	8	13	18·5	26	36	98·5
C.c. $N/100$-Na$_2$S$_2$O$_3$	30·1	28·5	27·0	26·3	25·9	25·5	25·5	25·5
Indene	14·4	16·0	17·5	18·2	18·6	19·0	19·0	19·0

Experiment IV. $C_0 = 18·115$; C_0 indene $= 26·50.$

t (mins.)	2	3·5	6·75	12	23·3	32·3	48·5	103
C.c. $N/100$-Na$_2$S$_2$O$_3$	16·6	15·0	14·15	13·5	12·8	12·5	12·4	12·4
Indene	27·9	29·5	30·4	31·0	31·7	32·0	32·1	32·1

It is apparent from these results that the indene compound dissociates slowly to reach an equilibrium corresponding to about 70% decomposition.

Formation of the Compound in Solution.—In order to show that the same position of equilibrium is reached when the components unite as when the compound dissociates, the nitro-ester and indene in quantities equivalent to the weight of compound in Expt. I were made up to the same molar concentration as in that experiment. Free indene was determined in 10-c.c. portions at successive intervals of time by the addition of 5 c.c. of 0·186N-bromine in carbon tetrachloride, excess bromine being found in terms of $N/100$-thiosulphate. Results are given below (Expt. V), and the data for decomposition and combination (Expts. I and V) are plotted in the figure.
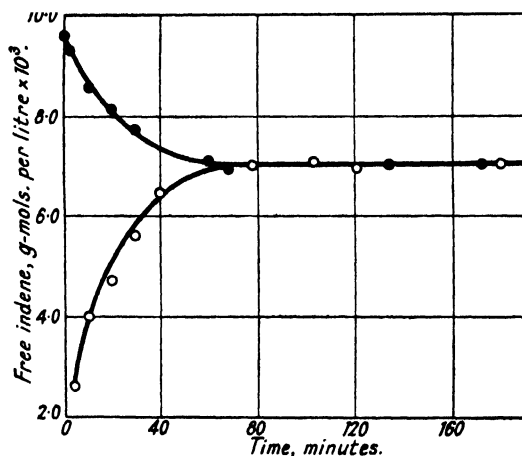
Experiment V. C_0 ester $= 19·20$; C_0 indene $= 9·60.$

t (mins.)	2	10·25	20·5	28·8	51	70	134	173
C.c. $N/100$-Na$_2$S$_2$O$_3$	74·4	75·9	76·6	77·6	78·8	79·2	79·0	79·0
Indene	9·8	8·55	8·2	7·7	7·1	6·9	7·0	7·0

Slow formation of the complex in presence of excess of indene is shown in Expt. VI.

Experiment VI. C_0 ester $= 66·60$; C_0 indene $= 56·19.$ 5 C.c. portions with 5 c.c. of 0·1244N-bromine.

t (mins.)	6	8	13	20	27·5	38·8	46·3	94·3
C.c. $N/100$-Na$_2$S$_2$O$_3$	21·3	25·6	28·1	30·4	31·0	31·2	31·2	31·2
Indene	40·9	36·6	34·1	31·8	31·2	31·0	31·0	31·0

DISCUSSION.

The experimental results described above show that when the crystalline complex containing 2 mols. of methyl $4:6:4':6'$-tetranitrodiphenate to 1 mol. of indene is dissolved in carbon tetrachloride at 38°, free indene is slowly produced, but that it slowly disappears when the two compounds are mixed in this solvent. Further, it has been established that the same position of equilibrium is reached from either direction. From these facts we can conclude that combination in the strict chemical sense takes place in this particular case. Also, from the fact that the complex in solution does not react with bromine under conditions in which indene readily reacts, we can infer that the ethylenic linkage in the combined indene is no longer able to function as a centre of unsaturation towards bromine, and is therefore a point of attachment of a molecule of nitro-ester.

It is improbable on general grounds that the tetranitrodiphenic ester reacts in solution by a termolecular process to produce ternary molecules N_2I, corresponding to the molecular composition of the solid complex. (N and I represent molecules of ester and indene respectively.) The most likely course of the interaction is a primary addition of nitroester to the reactive ethylenic linkage of the indene molecule (which must be the process upon which the method used to analyse the reacting systems depends), succeeded by the addition of a second molecule of nitro-compound. We should then have in solution the following equilibria: (i) $N + I \rightleftharpoons NI$; (ii) $NI + N \rightleftharpoons N_2I$. Seeing that the only molecular species in solution that can be estimated directly is the free indene, it is not possible to compute separately the concentrations of the two compounds NI and N_2I, and so to test the quantitative implications of the above equilibrium equations. However, the second molecule of nitro-compound is presumably attached to the more saturated benzenoid part of the indene molecule and is consequently less firmly held than the first. The actual concentration of N_2I molecules may therefore be small, their preferential separation from solution being due to their greater insolubility. If this view is accepted, conditions in solution will be controlled mainly by (i), and, from a knowledge of the initial concentrations and the amount of free indene present at equilibrium, approximate data can be obtained for evaluation of the equilibrium constant $K = [NI]/[N][I]$. Data and values for K are given in the following table, and it will be seen that a satisfactory constancy is obtained.

	Expt. I.	Expt. II.	Expt. III.	Expt. IV.	Expt. V.	Expt. VI.
$[NI] \times 10^3$	2·6	2·4	15·0	12·6	2·6	25·2
$[N] \times 10^3$	16·6	16·4	30·1	23·6	16·6	41·4
$[I] \times 10^3$	7·0	7·0	19·0	32·1	7·0	31·0
K	22	21	26	17	22	20

If the actual rates measured in Expts. I—VI are those of the decomposition and formation of the binary NI molecules, it should be possible to calculate the value of the equilibrium constant K from the initial rates of decomposition and combination. We thus find, from the first two amounts of free indene produced in Expts. I—IV, a mean unimolecular velocity constant $k_1 = 0·053$. From Expts. V and VI a mean bimolecular constant $k_2 = 1·0$ (0·8, 1·2) is obtained from the first points on the indene concentration-time curves. The ratio k_1/k_2 gives for the equilibrium constant K the value 18·9, which is in satisfactory agreement with the mean observed value 21.

A possible mode of attachment of the nitro-group to aromatic hydrocarbons has been discussed by Bennett and Willis (J., 1929, 256; see also Baker and Bennett, *Ann. Reports*,
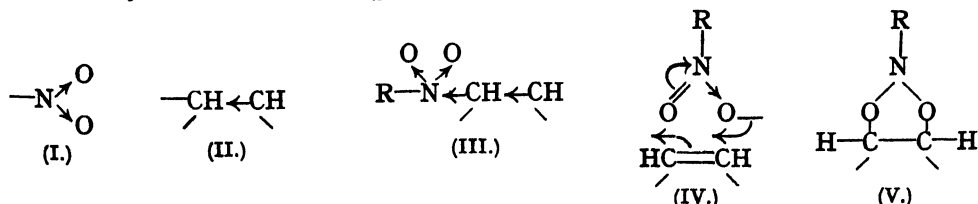
1931, 137), who suppose that the group functions in the kationoid form (I) and reacts with an ethylenic linkage in its polarised form (II) to give the structure (III). An alternative

process for the attachment of the nitro-group would be (IV), leading to (V). In this process the postulated recession of an electron pair from the doubly linked oxygen to the nitrogen is in the direction opposite to that in which polarisation of the $-N{=}O$ linkage is usually supposed to occur, and might not be expected to take place unless forced to do so by electron-attracting groups such as $-NO_2$, $-CO_2Me$, $-SO_2Cl$, etc., attached to the aromatic nucleus R. Bennett (*loc. cit.*) has pointed out that the presence of such groups is necessary before complexes of the type under discussion can be formed. The general instability of the complexes may tentatively be correlated with the fact that the above ring structure has hitherto not been associated with any known organic compound.

A decision between the two structures given above would seem to be possible on chemical grounds, since Bennett's formula indicates the presence in the molecule of a centre of kationoid reactivity. Preliminary experiments have failed, however, to give decisive evidence of such reactivity, and the question of structure must remain open until more definite experimental data are available.

SUMMARY.

A solid compound of methyl $4:6:4':6'$-tetranitrodiphenate (2 mols.) with indene (1 mol.) has been obtained, and found not to react with bromine in carbon tetrachloride solution. It has therefore been possible to follow the rate of formation and decomposition of the compound in solution. A state of equilibrium is reached, for which equilibrium constants have been evaluated on the supposition that, in solution, combined indene is mainly in the form of a binary compound with the nitro-ester.

129. *Studies in the Synthesis of Vitamin-*A. *Part I.*

By W. H. DAVIES, I. M. HEILBRON, W. E. JONES, and A. LOWE.

THE synthesis of ι-(2 : 2 : 6-trimethyl*cyclo*hexyl)-$\gamma\eta$-dimethyl-*n*-nonyl alcohol by Karrer, Morf, and Schöpp (*Helv. Chim. Acta*, 1933, **16**, 557; see also Karrer and Morf, *ibid.*, p. 625) and its identity with fully hydrogenated vitamin-*A* (perhydrovitamin-*A*) establish the structure (I) first proposed by Karrer, Morf, and Schöpp (*ibid.*, 1931, **14**, 1431) and supported by Heilbron, Morton, and Webster (*Biochem. J.*, 1932, **26**, 1199) for the vitamin.

$$H_2C\!\!\!<\!\!\!\begin{smallmatrix}CMe_2\\ \\CMe\end{smallmatrix}\!\!\!>\!\!C\text{-}[CH{:}CH{\cdot}CMe{:}CH]_2{\cdot}CH_2{\cdot}OH$$

(I.)

$$H_2C\!\!\!<\!\!\!\begin{smallmatrix}CMe_2\\ \\CHMe\end{smallmatrix}\!\!\!>\!\!CH{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2Br$$

(II.)
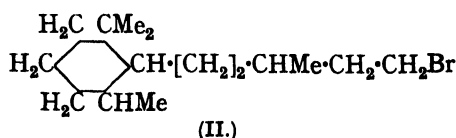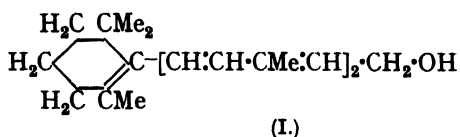
Prior to the first publication by Karrer, Salomon, Morf, and Walker (*Helv. Chim. Acta*, 1932, **15**, 878) relating to the synthesis of perhydrovitamin-*A*, we, working on a similar projected synthesis, had prepared ε-(2 : 2 : 6-trimethyl*cyclo*hexyl)-γ-methyl-*n*-amyl bromide (II), but further work in this direction was then abandoned. Karrer and Morf (*loc. cit.*) succeeded in condensing the above bromide with sodiomalonic ester, but all our attempts to condense it with sodioacetoacetic ester gave an unsaturated *hydrocarbon*, $C_{15}H_{28}$, probably ε-(2 : 2 : 6-trimethyl*cyclo*hexyl)-γ-methyl-Δ^α-pentene.

In the projected synthesis of vitamin-*A* itself, our first objective was α-aldehydo-δ-(2 : 2 : 6-trimethyl-Δ^6-*cyclo*hexenyl)-β-methyl-$\Delta^{\alpha\gamma}$-butadiene (III). As shown by Rupe and Gassmann (*Helv. Chim. Acta*, 1929, **12**, 198), tertiary acetylene carbinols of the type $RR'C(OH){\cdot}C{:}CH$ are capable in certain cases of rearrangement with formic acid to the isomeric $\alpha\beta$-ethylenic aldehydes (compare, however, Fischer and Löwenberg, *Annalen*, 1929, **475**, 186; Rupe and Hirschmann, *Helv. Chim. Acta*, 1931, **14**, 687). The *carbinol*

(IV) was therefore prepared by condensation of β-ionone with acetylene in presence of sodamide; * it reacted vigorously with formic acid or acetic anhydride, but no aldehyde could be detected among the products. The desired aldehyde was obtained from δ-(2 : 2 : 6-trimethyl-Δ⁶-*cyclo*hexenyl)-β-methyl-Δ^{α·γ}-butadiene-α-carboxylic acid (Karrer, Salomon, Morf, and Walker, *loc. cit.*) by an analogous method to that employed by Tiemann (*Ber.*, 1898, **31**, 826) for the preparation of citral from geranic acid : dry distillation of the barium salt of the acid with barium formate under reduced pressure gave a good yield of (III), characterised as its *phenylsemicarbazone*, m. p. 182—183°. Reduction of the aldehyde by the method of Reichstein, Ammann, and Trivelli (*Helv. Chim. Acta*, 1932, **15**, 264) gave the corresponding *alcohol*. This shows a broad inflexion in the ultra-violet absorption spectrum at about 270 mμ, but possesses no growth-promoting activity.

(III.)   R·CH:CH·CMe:CH·CHO   R·CH:CH·CMe:CH·CH:CH·COMe   (V.)

(IV.)   R·CH:CH·CMe(OH)·C:CH   R·CH:CH·CMe:CH·CH(OH)·CH₂·COMe   (VI.)

(VII.) R·CH:CH·CMe:CH·CH:CH·CH₂·OH   R·CH:CH·CMe:CH·CH(OH)·CH₂·CO₂Et   (VIII.)

$$\left(R = H_2C\overset{CH_2\cdot CMe_2}{\underset{CH_2-CMe}{<}}{>}C. \right)$$
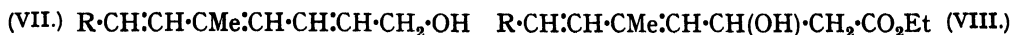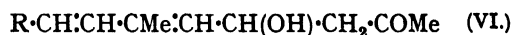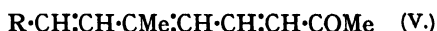
The condensation of (III) with acetone by means of hot piperidine (cold sodium ethoxide having proved unsatisfactory) gave the *hydroxy-ketone* (VI) (*phenylsemicarbazone*, m. p. 171—172°). The dehydration of this to (V) and the possibility of adding two more carbon atoms by the further application of the methods outlined above are under investigation.

In an attempt to prepare the alcohol (VII) with the view of ascertaining whether it would be physiologically active, the aldehyde (III) was condensed with ethyl bromoacetate to give *ethyl β-hydroxy-ζ-(2 : 2 : 6-trimethyl-Δ⁶-* cyclo*hexenyl)-δ-methyl-Δ^{γ·ε}-hexadiene-α-carboxylate* (VIII). As dehydration of this ester could not be effected under suitably mild conditions, it was hydrolysed, and the acid converted into the barium salt. This, when distilled with barium formate under reduced pressure, gave the original C₁₅-aldehyde (III), scission of the chain at the hydroxylated β-carbon atom evidently having occurred. This reaction is being further studied.

EXPERIMENTAL.

ε-(2 : 2 : 6-*Trimethyl*cyclo*hexyl*)-*γ-methyl-n-amyl Bromide* (II).—Our method of preparation (compare Karrer, Salomon, Morf, and Walker, *loc. cit.*) consisted in the condensation of tetrahydroionone with ethyl bromoacetate to ethyl β-hydroxy-δ-(2 : 2 : 6-trimethyl*cyclo*hexyl)-β-methylvalerate, which, as observed by the above investigators also, could not readily be dehydrated. It was therefore converted into the corresponding β-bromo-ester which was reduced with zinc dust and hydrogen chloride in acetic acid to ethyl δ-(2 : 2 : 6-trimethyl*cyclo*hexyl)-β-methylvalerate. Reduction of this with sodium and amyl alcohol gave ε-(2 : 2 : 6-trimethyl-*cyclo*hexyl)-γ-methyl-*n*-amyl alcohol as a slightly viscous oil, b. p. 136°/1·5 mm. (Karrer, Salomon, Morf, and Walker, *loc. cit.*, give b. p. 150—156°/7 mm.).

The bromide (II) was prepared by slowly adding a solution of the alcohol (16·5 g.) in dry petroleum (b. p. 80—100°; 40 c.c.) to phosphorus tribromide (10 g.) in the same solvent (40 c.c.). The whole was refluxed for 3 hours and, after cooling, poured into ice-water. The bromide was isolated by ether extraction and obtained as a pale yellow oil (15·5 g.), b. p. 140—145°/4 mm. (Found : C, 62·7; H, 10·0; Br, 27·5. Calc. for C₁₅H₂₉Br : C, 62·3; H, 10·1; Br, 27·7%).

*Condensation of ε-(2 : 2 : 6-Trimethyl*cyclo*hexyl*)-*γ-methyl-n-amyl Bromide* (II) *with Acetoacetic Ester.*—Alcoholic sodioacetoacetic ester (prepared from 10 g. of ethyl acetoacetate) was treated at 0° with the freshly distilled bromide (15·2 g. in 30 g. of alcohol). After remaining at this temperature for 2 hours, the mixture was refluxed for 12 hours and cooled. Ether extracted an oil which gave on distillation a pale yellow, mobile liquid (8 g.) with a pleasant terpene-like odour, b. p. 112—115°/2 mm. (Found : C, 86·2; H, 13·1. C₁₅H₂₈ requires C,

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* Since this synthesis was carried out, Gould and Thompson (*J. Amer. Chem. Soc.*, 1935, **57**, 340) also have prepared this compound. They used potassium *tert.*-amyloxide as condensing agent, having, contrary to our findings, failed to achieve reaction with sodamide.

86·5; H, 13·5%). The same product was obtained when the sodioacetoacetic ester was prepared in benzene, and the condensation carried out in this solvent.

Condensation of β-Ionone with Acetylene.—A solution of β-ionone (90 g.) in dry ether (150 c.c.) was added during ½ hour with stirring to a suspension of fresh sodamide (45 g.) in dry ether (220 c.c.), the whole being maintained at 0° for, in all, 2½ hours; acetylene was then rapidly passed into the viscous mass during 20 hours. The deep red mixture was poured on ice and ether-extracted. Removal of the solvent from the washed (dilute sulphuric acid) and dried extract, and distillation, yielded ε-(2 : 2 : 6-*trimethyl*-Δ⁶-*cyclohexenyl*)-γ-*methylpent-δ-en-α-yn-γ-ol* (IV) as a viscous yellowish oil (58 g.), b. p. 112—115°/3 mm., which gave an intense blue colour with chloroformic antimony trichloride, and readily formed a white silver salt (Found : C, 82·4; H, 10·2. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%).

α-*Aldehydo*-δ-(2 : 2 : 6-*trimethyl*-Δ⁶-*cyclohexenyl*)-β-*methyl*-Δ^{αγ}-*butadiene* (III).—Undistilled δ-(2 : 2 : 6-trimethyl-Δ⁶-*cyclo*hexenyl)-β-methyl-Δ^{αγ}-butadiene-α-carboxylic acid (46 g.), prepared as described by Karrer, Salomon, Morf, and Walker (*loc. cit.*), was converted into the potassium salt with aqueous potassium hydroxide (11·6 g. in 100 c.c. of water), and a solution of barium chloride (21·6 g. in 120 c.c. of water) slowly added with stirring. The precipitated barium salt was washed with water and dried by distilling its suspension in benzene under reduced pressure. A finely sieved mixture of the dry salt (29 g.) and barium formate (24 g.) was diluted with an equal bulk of silver sand and heated first for 1 hour (oil-bath temp. 150°) under 2 mm. pressure, and then directly by a luminous flame, until no more oil distilled over (about 1½ hours; wt. of distillate, 14·6 g.). The aldehyde was obtained after repeated fractionation as a pale yellow, mobile oil (11·7 g.), b. p. 92—93°/1·8 mm. It was volatile in steam, reduced Tollens's reagent, and rapidly formed a semi-solid semicarbazone and a red 2 : 4-dinitrophenylhydrazone, neither of which was suitable for characterisation, the former owing to excessive solubility and the latter because it could not be crystallised unchanged. The *phenylsemicarbazone*, prepared in the usual manner, separated from alcohol in needles, m. p. 182—183° (Found : C, 75·2; H, 8·2; N, 12·1. $C_{22}H_{29}ON_3$ requires C, 75·2; H, 8·3; N, 11·9%). The aldehyde, regenerated on treatment with oxalic acid and steam-distilled, showed a broad inflexion between 280—310 mμ, and gave a red-brown colour with antimony trichloride showing a band near 467 mμ and strong absorption in the violet region.

ε-(2 : 2 : 6-*Trimethyl*-Δ⁶-*cyclohexenyl*)-γ-*methyl*-Δ^{βδ}-*pentadien-α-ol*.—A solution of the above aldehyde (12 g.) and aluminium *iso*propoxide (12 g.) in absolute *iso*propyl alcohol (150 c.c.) was refluxed for 50 hours, the solvent removed, and the residue steam-distilled in a current of nitrogen. An ethereal extract of the distillate yielded an oil, which was treated with phenyl-semicarbazide acetate to remove unchanged aldehyde and again steam-distilled in nitrogen after 12 hours. The oily distillate was fractionally distilled, giving the *alcohol* as a pale yellow oil (8·5 g.), b. p. 99—100°/2 mm. [Found : C, 81·5; H, 10·7. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9%. Found, active hydrogen atoms, 0·98 (Zerewitinov)]. Chloroformic antimony trichloride and a few drops of acetic anhydride gave a red colour, slowly changing to blue-violet. No solid derivative of the alcohol has so far been obtained.

Ethyl β-*Hydroxy*-ζ-(2 : 2 : 6-*trimethyl*-Δ⁶-*cyclohexenyl*)-δ-*methyl*-Δ^{γε}-*hexadiene*-α-*carboxylate* (VIII).—A solution of the aldehyde (10 g.) and ethyl bromoacetate (9 g.) in dry benzene (30 c.c.) was added during ½ hour to zinc needles (4·0 g.) covered with boiling benzene (30 c.c.). The mixture was refluxed for 3 hours, and the filtered solution decomposed by shaking with 10% acetic acid (50 c.c.) for 2 hours. The whole was extracted with light petroleum (b. p. 40—60°) and the extract dried over sodium sulphate. The oily residue after removal of the solvent was distilled under reduced pressure, and the *ester* collected as a pale yellow oil (7·5 g.), b. p. 138—140°/2 mm. (Found : C, 74·2; H, 10·1. $C_{19}H_{30}O_3$ requires C, 74·5; H, 9·8%).

The ester (20 g.) was hydrolysed in the cold with alcoholic potassium hydroxide (5 g. in 75 c.c. of alcohol) and the red solution after dilution with water was thoroughly extracted with ether. The aqueous layer was rendered slightly acid with dilute phosphoric acid and extracted with ether, the extract washed and dried over sodium sulphate, and solvent removed. The oily acid was without further purification converted into its barium salt (yield, 14 g.), and heated with barium formate exactly as described under (III). The orange-yellow distillate was re-distilled and yielded a pale yellow oil, b. p. 95—97°/2 mm., which was proved to be identical with α-aldehydo-δ-(2 : 2 : 6-trimethyl-Δ⁶-*cyclo*hexenyl)-β-methyl-Δ^{αγ}-butadiene by conversion into the phenylsemicarbazone (feathery needles from alcohol), m. p. 182—183° alone or mixed with the phenylsemicarbazone of (III) (Found : N, 11·9. Calc. for $C_{22}H_{29}ON_3$: N, 11·9%).

β-*Keto*-δ-*hydroxy*-θ-(2 : 2 : 6-*trimethyl*-Δ⁶-*cyclohexenyl*)-ζ-*methyl*-Δ^{αη}-*octadiene* (VI).—A solution of the aldehyde (III) (11 g.) in a mixture of dry acetone (50 c.c.) and freshly distilled

piperidine (25 c.c.) was refluxed for 100 hours, a further quantity of piperidine (10 c.c.) being added after 40 hours. The excess of acetone and the piperidine were distilled off and the residue was steam-distilled in nitrogen. The distillate was extracted with ether; the washed and dried extract on distillation yielded an orange-yellow oil, b. p. 90—115°/2 mm., which was further separated into two fractions : (i) 3 g., b. p. 90—105°/2 mm., containing unchanged aldehyde, and (ii) 5 g., b. p. 109—111°/2 mm. Analysis of the latter after refractionation (b. p. 104—105°/1·5 mm.) proved it to be the *hydroxy-ketone* (Found : C, 78·0; H, 10·1. $C_{18}H_{28}O_2$ requires C, 78·2; H, 10·1%). The *phenylsemicarbazone* crystallised from alcohol in fine needles, m. p. 171—172° (Found : C, 73·4, 73·45; H, 8·4, 8·4; N, 10·5, 10·5. $C_{25}H_{35}O_2N_3$ requires C, 73·4; H, 8·5; N, 10·3%).

130. *The Factors determining the Velocity of Reactions in Solution. Molecular Statistics of the Esterification of Carboxylic Acids.*

By C. N. HINSHELWOOD and A. R. LEGARD.

As is now generally recognised, there are well-marked correlations between the energy of activation of a gaseous reaction and the absolute rate, which can, indeed, not infrequently be calculated fairly accurately from the simple formula $Ze^{-E/RT}$, Z being the collision number ("Kinetics of Chemical Change," Oxford, 1933, Chap. 3). Christiansen (*Z. physikal. Chem.*, 1924, **118**, 35) applied the formulæ of the kinetic theory to a few bimolecular reactions in solution and found that the rates calculated on the basis of analogy with the simplest gas reactions were several powers of ten greater than those observed. He mentioned as one possibility that the solvent exercised a specific deactivating influence, an idea which was taken up by Norrish and Smith (J., 1928, 129). Moelwyn-Hughes and Hinshelwood (J., 1932, 230) showed that certain typically slow reactions in solution did not take place any faster in the absence of the solvent, and, moreover, that the decomposition of chlorine monoxide (*Proc. Roy. Soc.*, 1931, A, **131**, 177), which has a normal rate in the gas phase (Hinshelwood and Hughes, J., 1924, **125**, 1841), takes place at the same rate and with the same activation energy in carbon tetrachloride solution. Thus the slowness of the reactions discussed by Christiansen must be inherent in their chemical nature rather than a function of the solvent. This idea is supported by the existence of a few examples of gas reactions with rates much smaller than the activation rate indicated by the simple formula (*e.g.*, Kistiakowsky and Nelles, *J. Amer. Chem. Soc.*, 1932, **54**, 2208). The work on chlorine monoxide showed that the formulæ for collisions between gas molecules could be applied with reasonable accuracy to the calculation of collisions between molecules of a solute, since it is very unlikely that such a compensation of effects would occur as to leave both the rate of reaction and the activation energy unchanged, if the collision number had been seriously changed by the solvent.

Moelwyn-Hughes ("Kinetics of Reactions in Solution," Oxford, 1933) then found in the literature a number of examples of reactions in solution where the rate is in fact given quite closely by the simplest formula, and it was pointed out by Grant and Hinshelwood (J., 1933, 258) that, of the known examples, nearly all which satisfy this formula are reactions in which an ion takes part. They suggested the desirability of exploring the hypothesis that in the expression $P . Z . e^{-E/RT}$ the value of P approaches unity when one of the reacting species is an ion, but tends to be several powers of ten smaller for reactions between undissociated molecules. Following this up, they found that for the reactions (*ibid.*) of ethyl chloride, bromide, or iodide with potassium hydroxide P is nearly unity,

while for the benzoylation of aniline it is very much smaller (*ibid.*, p. 1351). Williams and Hinshelwood (J., 1934, 1079) later showed that this conclusion still held even if the reaction of the amine with the acid chloride is a termolecular change involving a molecule of the solvent.

Quantum mechanics predicts the possibility, though not the inevitability, of chemical reactions with rates governed by transformation probabilities independent of temperature but profoundly modifiable by perturbing forces of an electrical nature. This suggested (J., 1933, 1357) that it might be profitable to explore the question of how far variations in E represented the operation of classical factors on reaction velocity, and variations in P that of quantum mechanical factors; *e.g.*, how far the high value of P in ionic reactions, or the influence of polar solvents, might depend upon the modification of a transformation probability by an electric field. Pursuing this idea, Williams and Hinshelwood (J., 1934, 1079) studied the influence of polar substituents in aniline and in benzoyl chloride on the rate of benzoylation, to find out whether the electron-displacement effects of organic chemistry would be represented by large changes in P. They found, however, a rather striking correlation between the changes in rate and the changes in E, in spite of the fact that P was as small as 10^{-7}. This was in agreement with Bradfield (*Chem. and Ind.*, 1932, **51**, 254), who had concluded that, in aromatic substitution, changes in activation energy were the important factors governing the rate. It seemed, therefore, that the smallness of P in the benzoylation reaction might be more reasonably attributed to the necessity for some very precise orientation of the molecules at the moment of reaction, but no definite conclusion could be reached without further evidence. On the other hand, marked variations in P came to light in the study of catalytic reactions. Rolfe and Hinshelwood (*Trans. Faraday Soc.*, 1934, **30**, 935) found that for the reaction of methyl alcohol with acetic acid catalysed by undissociated molecules of acetic acid P was of the order 10^{-7}, while Williamson and Hinshelwood (*ibid.*, p. 1145) found a value of 10^{-3} when the catalyst was the ion $CH_3 \cdot OH_2^+$. This led to the more extended investigation of the variations of P and E in esterification reactions, which is the subject of the experimental part of this paper. During the course of the work a paper by Smith (J., 1934, 1744) appeared dealing with the acetone–iodine reaction. He finds that the value of P for various acid catalysts is a function of their acid strength, an observation which seems analogous to that of the contrast between the molecule of acetic acid and the ion $CH_3 \cdot OH_2^+$, but, as will appear, the analogy does not prove to be as complete as might have been expected.

Kinetics of Esterification.—Esterification is, as far as we know, always a catalytic process, and is complicated kinetically by the fact that several of the molecular or ionic species present may be exerting independent catalytic effects. In the examples which we shall consider, the principal terms in the velocity equation are $-d[HX]/dt = k_0[HX][ROH_2^+] + k_1[HX]^2$, the alcohol, ROH, being the solvent and therefore of practically constant concentration. For a weak acid in presence of added hydrogen chloride, the first term so far outweighs the second that k_1 may be neglected and k_0 determined directly; k_1 can be determined by working in the absence of added hydrions at a fairly high temperature. In some of the examples, the reaction under these conditions becomes bimolecular with respect to the acid, and shows practically no retardation by small amounts of the sodium salt of the acid. The contribution of the hydrion-catalysed reaction must then be negligible, and k_1 is obtainable directly. When the addition of salt reveals an appreciable contribution from the hydrion-catalysed reaction, the appropriate corrections can be made by a suitable series of experiments with buffer solutions of varying concentration. At higher salt concentrations there may be an acceleration of the reaction in virtue of the catalytic effect of the anions. This, however, we are not directly concerned with. In general, there is little difficulty in isolating k_0 by working with added hydrogen chloride in the range 0—60°, and k_1 by working without added hydrions in the range 120—200°. It should be mentioned that the reaction between hydrogen chloride and aliphatic alcohols is rapid above 60°, having an energy of activation much higher than that with most organic acids. This fact limits the utility of hydrogen chloride as a catalyst, a matter which does not appear always to have been taken into account in the earlier work on esterification.

The method of measurement was that described by Rolfe and Hinshelwood and by

Williamson and Hinshelwood (*locc. cit.*). When k_1 is obtainable directly, it is calculated from the formula

$$kt = 1/(a - x) - 1/a \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and k_0 is obtained from the Goldschmidt formula

$$kct = (1 + a/r) \log_e a/(a - x) - x/r \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the units being g.-mols. per litre and seconds, and the subscripts being omitted since both k's are essentially the constants of a bimolecular process; r is a constant which allows for the retardation of the hydrion-catalysed reaction by water. The values for different temperatures used are those found by Williamson and Hinshelwood, Goldschmidt having shown that, for a given temperature, r is a function only of the alcohol and not of the acid; a is the initial concentration of the organic acid and c that of the hydrogen chloride. All concentrations were corrected for the expansion of the solvent, data from the International Critical Tables being used.

EXPERIMENTAL.

Preparation of Materials.—The alcohols were always used as the solvent. Methyl alcohol was prepared by the method of Hartley and Raikes (J., 1925, **127**, 524), involving dehydration by aluminium amalgam; benzyl and *iso*propyl alcohols were prepared by careful fractionation of the purest obtainable commercial products, and *tert.*-butyl alcohol was purified by freezing out five times from the melt and discarding the mother-liquor. Acetic acid was purified by repeated freezing out, trichloroacetic acid by distillation (distillation in a vacuum or at normal pressure gave the same result), and other acids by recrystallisation to correct m. p. and titre. For the specimen of 2 : 4 : 6-trimethylbenzoic acid we 'are very much indebted to Professor Robinson. Each reaction presents certain special problems, so that a separate note on each is necessary, but the final velocity constants for the different temperatures are all collected together in Table I. In all the systems the Arrhenius equation is followed within the limits of experimental error.

Reaction Catalysed by Undissociated Acid.—*Acetic acid and methyl alcohol.* This has already been studied by Rolfe and Hinshelwood (*loc. cit.*). Special means were adopted to isolate k.

Acetic acid and benzyl alcohol. This gives bimolecular constants. A typical series at 154·0° for a solution 1·00N at 25° is as follows :

t (mins.)	30	60	120	180	240
Change, %	13·5	23·4	37·8	48·3	54·4
$k \times 10^5$	8·67	8·47	8·44	8·65	8·28

The mean, $8·50 \times 10^{-5}$, corrected for the expansion of the solvent, becomes $9·49 \times 10^{-5}$. As might be expected from the minuteness of the dissociation of carboxylic acids in benzyl alcohol, the hydrion effect is negligible. Buffer solutions of $N/100$-sodium acetate produced no retardation, but a slight acceleration, of the reaction, amounting to 6·0% at 154° and to 3·5% at 100°.

Acetic acid and isopropyl alcohol. The buffer effect was very small, and constants could be calculated directly by formula (1). At 100°, $N/100$-salt caused retardation by 4·0% for N-acid.

Acetic acid and tert.-butyl alcohol. This reaction presents special difficulties. It is very slow except at temperatures within measurable distance of the critical temperature of the alcohol. The practical difficulty of the high pressure developed was overcome by the use of small, stout, sealed tubes, but a further complication arose from the fact that above 200° the reaction came to equilibrium when less than 10% of the acid was esterified, a fact which seemed strange, since with other alcohols the reaction went almost to completion. Moreover, the equilibrium constant seemed to change with temperature more rapidly than corresponded to the van 't Hoff equation unless an improbably high value were assumed for the heat of reaction. When, however, it was realised that the critical temperature of the solvent was being approached, and that the latent heat of one of the reactants was therefore tending to zero, it became clear that rapid changes in the heat of reaction itself were to be expected, and abnormal displacements of equilibrium would result, which would, indeed, be in the sense observed. The procedure adopted was therefore to measure very carefully the progress of the reaction up to about 10%, and to find the initial rate by drawing tangents. Thence k can be calculated. It is easy to show from the kinetic equations that the early attainment of equilibrium does not introduce any inaccuracy into the initial rate method, since the curves start with the right slope and only begin to suffer

rapid changes of curvature when equilibrium is fairly closely approached. Even at 100°, the buffer influence was small.

Benzoic acid and methyl alcohol. The contribution from the hydrion-catalysed reaction is smaller than with acetic acid. With N-solutions practically no correction is required over the range 100—150°. Bimolecular constants are obtained. These rise somewhat when the initial concentration is reduced to $N/5$ or to $N/20$. In the diluter solutions small concentrations of benzoate cause some retardation, and larger concentrations an acceleration.

	Initial concn.				Initial concn.		
Temp.	Acid.	Benzoate.	$k \times 10^7$.	Temp.	Acid.	Benzoate.	$k \times 10^7$.
153·1°	1·00	nil	111·2	100·0°	1·00	nil	5·11
	0·20	nil	123·9		0·20	nil	5·7
	0·05	nil	154·0				
	1·00	0·01	120·2		1·00	0·01	4·70

The following figures show the increase in speed produced by benzoate at higher concentrations, with $N/5$-acid : b = concentration of benzoate, v = initial rate, %, per 10^3 hours, and v' % per 10^3 minutes.

	100·0°.					153·1°.				
b	0·005	0·025	0·05	0·10	b	0·0	0·005	0·025	0·05	0·10
v	27·2	33·2	40·0	55·0	v'	10·5	10·5	15·0	24·0	36·3

By extrapolating the rising part of the curve of rate against benzoate concentration to zero concentration, we obtain the rate corrected for the hydrion effect. Further correcting this for expansion of the solvent, we find a value of 18,500 cals. for E. The effect of the buffer on the N-solutions is so small that the Arrhenius equation may be applied directly to the data in Table I, and a value 18,300 is found. The latter is adopted as the better value, since the experiments with N-solutions were more numerous, more accurate, and needed no extrapolation.

Benzoic acid and iso*propyl alcohol.* The influence of the sodium salt being small with acetic acid in isopropyl alcohol, and smaller with benzoic acid than with acetic acid in methyl alcohol, it was considered justifiable to make direct measurements with N-solutions.

Benzoic acid and tert.-*butyl alcohol.* The same special methods were necessary as with acetic acid and this alcohol.

Benzoic acid and benzyl alcohol. The temperature coefficient was determined directly with N-solutions. Sodium benzoate produces an acceleration.

o-*Nitrobenzoic acid and methyl alcohol.* The contribution of the hydrion-catalysed reaction here becomes considerable. Initial rates were measured for $N/5$-solutions with varying amounts of the sodium salt. At 153·7° :

Benzoate	0·0	0·0025	0·005	0·02	0·05	0·10
Relative initial rate	1·0	0·954	0·954	1·032	1·326	1·578

Extrapolating the rising part of the curve to zero concentration, we obtain a value of 0·92. The total velocity corresponds to a constant of $1·32 \times 10^{-5}$. Thus the corrected constant is $1·21 \times 10^{-5}$. A similar procedure at 100·0°, where the buffer influence is greater, gives a constant of $3·54 \times 10^{-7}$, whence $E = 20,700$. This value is less reliable than those obtainable more directly.

Diphenylacetic acid and benzyl alcohol. Since none of the other acids showed an important hydrion effect in benzyl alcohol, a series of direct readings were made with N-solutions.

Trichloroacetic acid in benzyl alcohol. Although it is a strong acid in water, trichloroacetic acid is extremely weak in benzyl alcohol, and catalysis by hydrions is very small compared with that by undissociated molecules. The reaction is much faster than with the other acids studied, and conveniently measurable over the range 20—80°. To leave no doubt about the mechanism of the process measured, rather fuller data are given. Variation of the initial concentration over a wide range shows the reaction to be bimolecular with respect to the acid. Thus at 35·1° we have :

a	1·224	0·791	0·443	0·318	0·170	0·0900	0·0503
$k \times 10^6$	7·34	6·70	6·30	6·37	6·38	6·66	6·80

For $a = 0·1634$ and sodium trichloroacetate = 0·01, $k \times 10^6$ was 6·20, and for $a = 0·1763$ and sodium trichloroacetate = 0·02, $k \times 10^6$ was 6·50. For a given initial concentration, the bimolecular formula gives constant values of k over a considerable range; they fall away only

when a rather high concentration of reaction product is reached. Thus at 35·1° the following typical results were obtained (a = 0·4426) :

Hours	7·3	12·0	22·25	34·6	53·6	78·2	102·8
Change, %	6·88	10·80	18·1	26·0	34·8	43·4	49·5
$k \times 10^6$	6·35	6·33	6·23	6·37	6·25	6·15	5·99

The values of k tabulated in Table I are mean values taken over the first third of the reaction. On account of the slight dependence on the initial concentration, values were found at each temperature for at least two concentrations, and that for a 0·50N-solution calculated by interpolation. The variation of k, however, is much too small to be of serious significance.

2 : 4 : 6-*Trimethylbenzoic acid in benzyl alcohol.* At first, it appeared that no measurements would be possible, since the pure molten acid suffered extensive decarboxylation at temperatures high enough to give a measurable rate of esterification. In benzyl-alcoholic solutions, however, the decarboxylation appeared to be negligible compared with that occurring in the pure state, since no pressure of carbon dioxide developed in the small sealed tubes used, no smell of mesitylene was observed, and the reaction was of the second order. Decarboxylation reactions are known in many examples, including that of the analogous 2 : 4 : 6-trinitrobenzoic acid (*Proc. Roy. Soc.*, 1931, *A*, **131**, 186), to be of the first order. Thus we conclude that the actual rate of esterification is indicated by the rate of disappearance of the acid.

Temp. 279° $\begin{cases} a & 0·713 \quad 0·356 \quad 0·238 \\ k \times 10^5 \dots & 16·0 \quad 16·3 \quad 19·0 \end{cases}$ Temp. 240° $\begin{cases} a & 0·713 \quad 0·356 \\ k \times 10^5 \dots & 1·98 \quad 2·10 \end{cases}$

Reactions catalysed by Added Hydrions from Hydrogen Chloride.—*Benzoic acid and methyl alcohol.* The applicability of formula (2), already extensively tested by Goldschmidt, appears from the following figures for 25·0° :

a = 0·100, c = 0·020, r = 0·22; t' − time in minutes.

t'	0	230	1175	1670	3120	4605	7270
$(a - x)$	0·0996	0·0946	0·0768	0·0694	0·0511	0·0402	0·0258
$k \times 10^4$	—	1·89	2·00	1·93	1·99	1·89	1·91

Of the mean values given in Table I, that for the highest temperature had to be corrected for a small disappearance of hydrogen chloride by reaction with the alcohol during the course of the experiment.

Diphenylacetic acid and methyl alcohol. The course of the reaction is given by (2).

TABLE I.

Mean velocity constants at various temperatures.

Acetic acid. Benzyl alcohol. a = 1·00.		Acetic acid. isoPropyl alcohol. a = 1·00.		Acetic acid. tert.-Butyl alcohol. a = 1·00.		Benzoic acid. Methyl alcohol. a = 1·00.		Benzoic acid. isoPropyl alcohol. a = 1·00.	
Temp.	$k \times 10^6$	Temp.	$k \times 10^6$	Temp.	$k \times 10^7$	Temp.	$k \times 10^7$	Temp.	$k \times 10^7$
154·0°	94·9	183·6°	72·9	211·0°	83·5	153·1°	111·2	210·8°	404
140·3	58·2	154·4	23·2	182·6	18·1	138·7	56·1	183·3	91·2
119·2	20·8	139·2	11·9	153·7	5·95	120·3	17·1	153·4	17·0
100·6	7·10	118·6	4·49	140·3	2·86	100·0	5·11	139·2	8·49
		100·5	1·65	100·4	0·25				

Benzoic acid. tert.-Butyl alcohol. a = 1·00.		Benzoic acid. Benzyl alcohol. a = 1·00.		Diphenylacetic acid. Benzyl alcohol. a = 1·00.		Trichloroacetic acid. Benzyl alcohol. a = 0·500.		2 : 4 : 6-Trimethyl-benzoic acid. Benzyl alcohol. a = 0·587.	
Temp.	$k \times 10^8$	Temp.	$k \times 10^7$	Temp.	$k \times 10^6$	Temp.	$k \times 10^6$	Temp.	$k \times 10^7$
211·1°	88·5	153·7°	119·2	183·1°	108·2	78·2°	91·5	277·2°	1460
194·4	31·0	138·9	54·6	154·6	38·0	65·4	47·3	237·2	177
182·8	14·9	121·0	17·1	140·1	18·1	52·95	21·1	211·0	37·6
		100·0	4·24	119·1	6·73	35·1	6·42	183·3	7·7
				100·7	2·06	24·2	2·94		

Benzoic acid. Methyl alcohol. Hydrogen chloride.								Diphenylacetic acid. Methyl alcohol. Hydrogen chloride.	
Temp.	a.	c.	$k \times 10^5$	Temp.	a.	c.	$k \times 10^4$	Temp.	Mean $k \times 10^4$
0·2°	0·100	0·0100	1·67	50·6°	0·100	0·0100	152	0·0°	3·63
25·0	0·100	0·0100	19·0		0·100	0·0200	157	24·05	19·0
	0·100	0·0200	19·4	60·3	0·100	0·0100	303	34·0	33·6
40·0	0·100	0·0100	65·6					44·0	55·4
	0·100	0·0200	65·0					54·14	106·6

DISCUSSION.

General.—The values of the constants in the formula $\log_e k = A - E/RT$, together with the calculated values for the velocity constant at $100 \cdot 0°$, are given in Table II.

TABLE II.

Acid.	Alcohol.	Catalyst.	$A.$	$E.$	$k_{100°} \times 10^7.$
$CH_3 \cdot CO_2H$	$CH_3 \cdot OH$	$CH_3 \cdot CO_2H$	5·817	13,000	76·4
$C_6H_5 \cdot CO_2H$	$CH_3 \cdot OH$	$C_6H_5 \cdot CO_2H$	10·282	18,300	5·07
$o\text{-}NO_2 \cdot C_6H_4 \cdot CO_2H$	$CH_3 \cdot OH$	$o\text{-}NO_2 \cdot C_6H_4 \cdot CO_2H$	13·20	20,700	3·54
$C_6H_5 \cdot CO_2H$	$C_6H_5 \cdot CH_2 \cdot OH$	$C_6H_5 \cdot CO_2H$	12·054	19,750	4·19
$CH_3 \cdot CO_2H$	$(CH_3)_3C \cdot OH$	$CH_3 \cdot CO_2H$	7·943	18,830	0·24
$CH_3 \cdot CO_2H$	$C_6H_5 \cdot CH_2 \cdot OH$	$CH_3 \cdot CO_2H$	8·942	15,350	72·1
$CHPh_2 \cdot CO_2H$	$C_6H_5 \cdot CH_2 \cdot OH$	$CHPh_2 \cdot CO_2H$	9·061	16,350	21·0
$CH_3 \cdot CO_2H$	$(CH_3)_2CH \cdot OH$	$CH_3 \cdot CO_2H$	7·434	15,330	16·4
$C_6H_5 \cdot CO_2H$	$(CH_3)_2CH \cdot OH$	$C_6H_5 \cdot CO_2H$	11·879	21,150	0·528
$C_6H_5 \cdot CO_2H$	$(CH_3)_3C \cdot OH$	$C_6H_5 \cdot CO_2H$	14·745	27,500	0·00171
$2:4:6\text{-}C_6H_2Me_3 \cdot CO_2H$	$C_6H_5 \cdot CH_2 \cdot OH$	$C_6H_2Me_3 \cdot CO_2H$	16·481	27,700	0·00741
$CCl_3 \cdot CO_2H$	$C_6H_5 \cdot CH_2 \cdot OH$	$CCl_3 \cdot CO_2H$	9·580	13,130	2760
$CH_3 \cdot CO_2H$	$CH_3 \cdot OH$	$CH_3 \cdot OH_2{}^+$	14·448	10,200	$1 \cdot 89 \times 10^7$
$C_6H_5 \cdot CO_2H$	$CH_3 \cdot OH$	$CH_3 \cdot OH_2{}^+$	18·039	15,700	$4 \cdot 0 \times 10^5$
$CHPh_2 \cdot CO_2H$	$CH_3 \cdot OH$	$CH_3 \cdot OH_2{}^+$	12·067	10,800	$7 \cdot 8 \times 10^5$

The most convenient way of obtaining a general view of the changes in E and P from one reaction to another is to plot E against $\log k$ for a standard temperature. Since

FIG. 1.
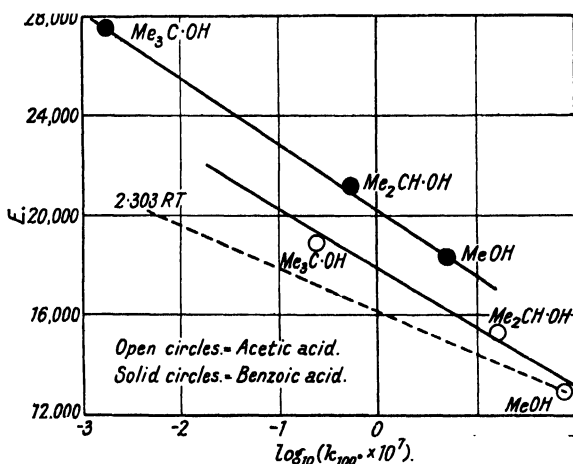
(number of molecules reacting) $= P \cdot Z \cdot e^{-E/RT}$, $\log_e k = \log_e C + \log_e P + \log_e Z - E/RT$, where C is a universal constant, for conversion of units. For the series of reactions under consideration, the variations of $\log_e Z$ will be neglected in a preliminary survey, since they depend upon changes in square roots of functions of the molecular weights and upon variations in molecular diameters, two factors which are small compared with others and partly compensate one another. Thus, if the difference in speed of two reactions is due entirely to changes in E, the two points on the graph will be connected by a line of slope $2 \cdot 303RT$. The actual slope of the line shows how far the changes in speed are due to changes in E and how far to changes in P.

In Fig. 1 the results for the reactions of acetic and benzoic acids severally with a primary, secondary, and tertiary aliphatic alcohol are shown. When change of alcohol decreases the velocity of esterification, whether of acetic or of benzoic acid, there is an increase in the activation energy even greater than that corresponding to the line of slope $2 \cdot 303RT$. Thus P is actually greater for the slower reactions.

Fig. 2 reveals a similar increase both in E and in P on passing from methyl to benzyl

alcohol, which is parallel with the increase in both factors on passing from acetic to benzoic acid.

Fig. 3 represents the results for a series of acids in benzyl alcohol, increases in E on passing from trichloroacetic acid through acetic acid to diphenylacetic acid almost entirely accounting for the changes in speed. For benzoic and trimethylbenzoic acids the values

FIG. 2.
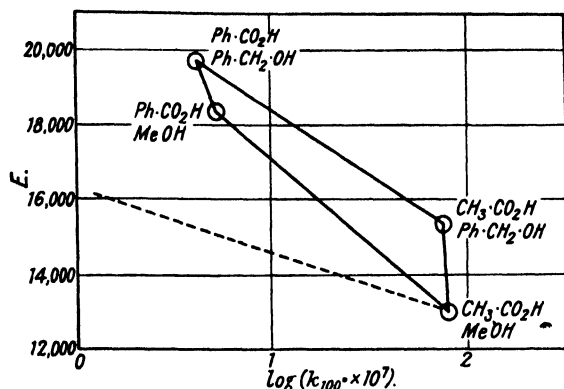
of E are again greater than corresponds to the decreased rates, so that P must have increased.

Fig. 4 shows the increase in P by several powers of ten when the hydrion replaces the undissociated acid molecule as the catalyst. Benzoic and acetic acids show nearly the same difference, the four points in the figure forming an approximately true parallelogram. The dotted lines have the slope $2\cdot303RT$.

FIG. 3.
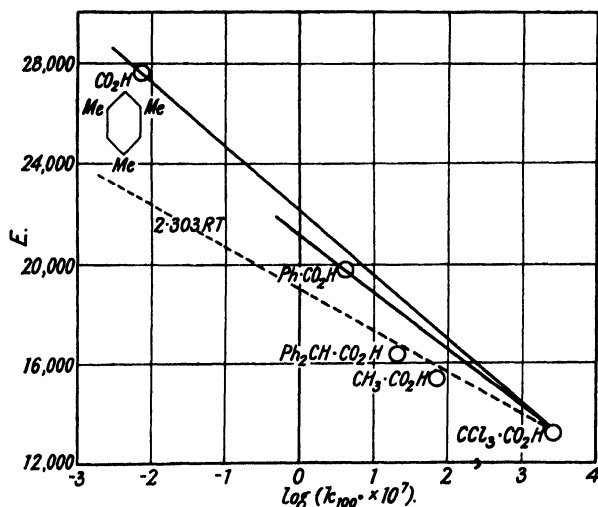
Processes involved in Ester Formation.—There is good evidence that when an ester is formed the hydroxyl and not the hydrogen of the carboxylic acid is replaced (cf. Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508). On the other hand, catalysis by another acid molecule may depend upon the transfer of a proton from the catalyst at some stage of the reaction. Rate of esterification might, therefore, be a function of the readiness with which the dismemberments (1), (2), and (3) occur. (2) and (3), involving the move-ment of a proton only, might depend upon a quantum-mechanical transition probability.

In so far as this was a controlling factor, the slowest reactions would be determined by small values of P rather than by large values of E.   In fact, the reverse is found, as has just

$$R\cdot CO\,|\,OH \qquad\qquad R\cdot O\,|\,H \qquad\qquad R\cdot COO\,|\,H$$
$$(1) \qquad\qquad\qquad (2) \qquad\qquad\qquad (3)$$
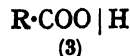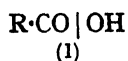
been shown.   If, therefore, the processes (2) and (3) determine the rate, their ease appears to be measured by the activation energy.

When the catalyst is a second molecule of the reacting acid, (1) and (3) will be oppositely influenced by polar substituents.   Thus, with trichloroacetic acid, (3) occurs more readily than with acetic acid, and (1), it may be presumed, correspondingly less readily.   Hence compensation may be expected, though to an unpredictable extent.   Actually, the reaction of trichloroacetic acid is more rapid than that of acetic acid.   It is important to observe, however, that the compensation reflects itself in the not very different value of E.   We do not find, as we might have done, that increased difficulty of (1) is reflected in an increased E while the increased ease of (3) leads to a correspondingly greater P.

So far, therefore, there is no positive evidence of the control of this reaction by quantum-mechanical transition probabilities.   Nor do the foregoing results correspond to those found by Smith for the influence of different acid catalysts on the rate of enolisation of acetone, there being little sign of a correlation between the values of P of the acids and their acid strengths in water.   We do, however, find that in the extreme case of replacement of the undissociated molecule by the hydrion, P increases by about 10^4.   Whether this really depends upon the greater ease of proton transfer or whether it depends upon the powerful orientating influence of the charged ion in contrast with the undissociated molecule, is a matter for further experiment.

FIG. 4.

Absolute Magnitude and Nature of P.—The foregoing conclusions are to a large extent independent of the absolute value of P.   To determine this it is necessary to satisfy ourselves that collision numbers in solution can be calculated correctly, at least as regards order of magnitude, and to know what correction, if any, must be applied to the observed energy of activation to allow for the variation with temperature of solvent–solute collisions.   Under the conditions of these experiments, acid and catalyst must meet in presence of a suitable solvent molecule.   That the ordinary formulæ for collisions between gas molecules are applicable, at least approximately, to the collisions between two solute molecules is indicated both by theoretical considerations and by the experimental results for chlorine monoxide (see p. 587).   Collisions between solute and solvent are more difficult to treat.   The number diminishes as the temperature rises, on account of the relatively rapid increase in the free space in the liquid as the total volume expands.   The decrease in viscosity with rise in temperature runs parallel with this and may be due partly to the same cause.   According to Jowett's formula (cf. Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1933, p. 159), the appropriate correction to make to the observed value of E is to add Q obtained from the formula $-d\log_e\eta/dT = Q/RT^2$.   How far this correction is valid in general, or necessary in the present example, is a matter of some uncertainty, but when it is applied, the absolute value of P for the reaction between acetic acid and methyl alcohol catalysed by undissociated acetic acid is found to be of the order 10^{-7}.   If the correction is omitted, the value is between 10^{-8} and 10^{-9}.   Since Z will not vary seriously,

$\log_e P$ will be proportional to A of Table II, whence we find that the greatest value of P, for methyl alcohol, benzoic acid, and hydrion, is about 3×10^{-2}, with the viscosity correction (and 10—10^2 times smaller without). The other values range between the above limits. The highest values of P could quite easily be accounted for by the necessity for a correct orientation of the molecules at the time of reaction. The lowest are perhaps surprisingly small to be accounted for in this way, although the three molecules of alcohol, acid, and catalyst may have to arrange themselves in a delicately adjusted geometrical pattern before reaction can occur (and this adjustment may be rendered much easier by the presence of a charged ion).

Correlation between P *and* E.—Figs. 1—3 all show a quite definite increase of P with E. The slowest reactions are not slow because P is small, but because E is large, and indeed, when E is large P is also large. For systems, therefore, which only become reactive when supplied with a large excess of energy, the factor which normally renders the collisions inefficient appears to control the situation to a much smaller extent. Possible explanations are not difficult to invent. When a molecule is dislocated by violent internal vibrations, its exact orientation may well become of less consequence. Or again, a high degree of activation may cause such electrical polarisation that a transition probability, otherwise small, tends towards unity. Choice among these and other possibilities must await further experiment.* (It may be pointed out that the viscosity corrections for methyl, *iso*propyl, *tert.*-butyl, and benzyl alcohols are respectively 2480, 5100, 6500, and 5050 calories, and, if they were applied to the values in Figs. 1—3, they would exaggerate rather than explain away the correlation between high E and high P values.)

Nature of Steric Hindrance.—The diminution in rate on passing from primary through secondary to tertiary alcohols, from methyl to benzyl alcohol, from acetic to benzoic acid, and especially from benzoic acid to $2:4:6$-trimethylbenzoic acid, exemplifies what is often called steric hindrance. It is of interest to note that the diminution is not due to decrease of P. Hence steric hindrance is energetic rather than geometrical in nature. The only example among those studied where there is not an actual increase in P for the sterically hindered reaction is on passing from acetic to diphenylacetic acid with hydrion as a catalyst in methyl alcohol : E increases by 600 cals. and P decreases by about one power of ten.

Conclusion.—In conclusion, it may be useful to summarise some information now available about the factor P for reactions in solution.

(1) It varies over the range 10^{-9} to unity. (2) When one of the reacting species is a charged ion, it tends to approach unity, sometimes rather closely. (3) There are examples, though rather less common than might have been expected, where it rises much above unity, on account, presumably, of the participation of internal degrees of freedom, as with unimolecular gas reactions of complex molecules. These cases do not seem to be common enough to invalidate the statement that unity is the limiting value for an important class. (4) Polar substituents in the benzene ring may produce great changes in velocity by changing the activation energy without affecting P to a degree comparable in importance,

* If the energy of activation is distributed among many degrees of freedom, P may assume a value far greater than unity (" Kinetics of Chemical Change in Gaseous Systems," 3rd edition, p. 187). On the other hand, the necessity for the redistribution of the energy to the appropriate parts of the molecule tends to reduce P. With unimolecular gas reactions, the first factor nearly always seems to predominate, but in certain circumstances the second might. If we had a change in mechanism from one involving direct activation in, say, one degree of freedom to one involving several degrees of freedom and an internal redistribution, then we might easily have an increase in E and a corresponding increase in P. Something of this kind is observed in certain catalytic reactions (*op. cit.*, p. 227). Where the collisions are such as to place the energy directly in the vital bond we have the low-E type, but where the vital bond is, as it were, shielded, much more energy must be put into the molecule, in order that some of it may find its way to the right place. But the increased variety of activated states now possible increases P very greatly. This effect might be superimposed on a geometrical condition making P tend to be small, and we should have the state of affairs under consideration in the present paper. The part which such factors may play in reactions in solution is under experimental investigation, but for the moment it seems preferable to see how much progress can be made without introducing this complication.

even when P itself is very small.   (5) Steric hindrance depends upon E rather than upon P.   In esterification, (6) changes in the alcohol or the reacting acid modify the rate according to their effect on E, (7) P tends to increase with E, (8) on changing from a non-ionic catalyst to the hydrion, P increases by about 10^4, but differences between undissociated acid catalysts seem to depend mainly upon E, in contrast with what has been found for the enolisation of acetone.

SUMMARY.

From the study of the rates and energies of activation of 15 esterification reactions, the following conclusions are reached.

(1) For a series of alcohols, changes in rate are determined by variations in the activation energy, not by the constant P in the formula : Rate $= P \cdot Z \cdot e^{-E/RT}$.

(2) Similarly, for a series of acids, those which react most slowly correspond to the highest values of E.

(3) In general, there is a correlation between large values of E and large values of P and *vice versa*.

(4) On changing from a non-ionic catalyst to the hydrion, there is an increase of P of about 10^4, but differences between various non-ionic catalysts seem rather to depend upon the values of E itself.

(5) Steric hindrance appears to depend upon high activation energy, rather than to be of a purely geometrical character.

(6) The results provide no positive evidence that the rate of esterification reactions depends upon quantum-mechanical transition probabilities, or that the smallness of P in such reactions is connected with the smallness of such probabilities, rather than with the necessity for a delicately adjusted orientation of the molecules at the moment of reaction.

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131. *The Kinetics of the Decomposition of Diphenyliodonium Iodide.*

By C. J. M. FLETCHER and C. N. HINSHELWOOD.

DIPHENYLIODONIUM iodide is known to decompose on heating into iodobenzene according to the equation $(C_6H_5)_2I\cdot I = 2C_6H_5I$.   The study of the kinetics of this reaction is somewhat difficult on account of the small solubility of the iodide in nearly all solvents.   It has been found possible, however, to study the decomposition both in the solid state and in solution in iodobenzene, by starting with a weighed amount of the solid, and estimating the amount of diphenyliodonium iodide which remains unchanged at different times.   Under these conditions the decomposition is autocatalytic, which indicates that there is a much more rapid decomposition of the iodide that dissolves in the iodobenzene formed.   As the reaction proceeds, the amount of iodobenzene increases and, therefore, more diphenyliodonium iodide goes into solution.   Since the solubility is of the order of 1 mol. per 1000 mols. of iodobenzene, excess of the solid is present until the decomposition is nearly complete.

The curve obtained by plotting percentage decomposition against time can be interpreted as follows.   If a be the weight in grams of diphenyliodonium iodide originally present, and x the weight decomposed after time t, the amount of iodide in solution is sx, where s is the solubility, expressed as g. of solute per g. of solvent.

Then
$$dx/dt = -d(a-x)/dt = k_1(a-x) + k_2 sx.$$

Hence
$$t = \frac{1}{(k_2 s - k_1)} \log_e \frac{k_1 a + x(k_2 s - k_1)}{k_1 a}.$$

On the assumption, subsequently justified, that $k_2 s$ is much greater than k_1, we have
$$t = (1/k_2 s) \log_e \{(k_1 a + k_2 sx)/k_1 a\}.$$

After the initial stage of the reaction, $k_2 s/k_1$ will be great compared with a/x, so that

$$t = (1/k_2 s)(\log_e x/a + \log_e k_2 s/k_1) \quad \ldots \ldots \ldots \quad (1)$$

If the logarithm of the proportion changed, x/a, is plotted against time, a linear relationship should hold after the very first stages irrespective of the initial weight. The slope of the line is $k_2 s$: from the value, t', of the time at which $x/a = 1$, and $\log_e x/a = 0$, k_1 may be found from the equation

$$t' = (1/k_2 s) \log_e k_2 s/k_1 \quad \ldots \ldots \ldots \ldots \quad (2)$$

EXPERIMENTAL.

Diphenyliodonium iodide was prepared in the usual manner from iodobenzene. Estimation as iodide, by dissolving it in aqueous alcohol and titrating by Volhard's method, gave results exceeding 99% of the calculated.

A number of tubes containing a weighed quantity of the substance were sealed and placed in a thermostat. After a suitable time a tube was removed, and the contents dissolved in aqueous alcohol and analysed for unchanged iodide. A small quantity of free iodine was formed, but it amounted at the end of the reaction to less than 0·5% of the original diphenyliodonium iodide.

Electrically controlled thermostats were used below 100°, and vapour baths for the higher temperatures. The variations in temperature did not in general exceed 0·1°.

The solubility of diphenyliodonium iodide in iodobenzene was too small to be determined by the usual methods. A conductivity method was therefore adopted. A saturated solution was prepared at a given temperature, and rapidly forced through a Jena-glass filter into a weighed flask containing a known volume of conductivity water. The flask was shaken long enough to ensure complete partition of the diphenyliodonium iodide between the two solvents. The greater part passed into the aqueous layer, the partition coefficient at room temperature being approximately 10. The conductivity of the aqueous solution was determined by means of a Leeds and Northrup S.P. 929 bridge and A.C. galvanometer, type 2470(c). The limiting equivalent conductivity * of diphenyliodonium iodide was taken as 103, the sum of the ionic mobilities. Blank experiments in which water was shaken with iodobenzene were carried out, and corrections made accordingly. The iodobenzene used was dried with calcium chloride and distilled at 3 mm. pressure. From the measured conductivity the quantity of iodide originally present in the iodobenzene solution could be calculated. Allowance was made for the change in the equivalent conductivity with the concentration of the aqueous solution. Since diphenyliodonium iodide undergoes a photochemical decomposition, the solutions were protected from light.

Results.—The reaction was studied at five temperatures such that the time for complete reaction varied by a factor of 100 from just over 1 hour to nearly 5 days. Table I shows the course of the decomposition at 111·3°. Col. 3 shows that, from 10% decomposition onwards, a linear relation holds between $\log x/a$ and t, in agreement with equation (1).

Table II summarises the results at different temperatures: $k_2 s$ and $\log_{10} k_1$ are calculated from equations (1) and (2). Both k_1 and k_2 are in reciprocal hours. When plotted against the reciprocal of the absolute temperature, $\log_{10} k_2 s$ and $\log_{10} k_1$ conform to the Arrhenius equation, except in the case of $\log k_1$ at the highest temperature. It may be noted that, at the temperatures used, $k_2 s$ is always more than 10 times, and at 120° more than 100 times, greater than k_1. Two sources of error should be considered. (*a*) In estimating the time no allowance was made for that taken by the tube to reach the temperature of the thermostat. The error thus introduced does not affect the value of $k_2 s$, which depends only upon the slope of the $\log x/a$–t line. It will, however, influence the value of t', and will be most serious at the highest temperature where t' is smallest. This may account for the low value of t' at 120·2°, for, if at this temperature t' is 1·00 and not 1·15 hrs., the value of k_1 agrees with that calculated from lower temperatures. (*b*) It has been assumed that all the iodobenzene present remains saturated with diphenyliodonium iodide as long as any solid is present. Any departure from this condition will make the observed values of $k_2 s$ and k_1 lower than the true values. Saturation is more likely to be maintained during the slower reactions. Thus the observed activation

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* The conductivity of iodonium salts has been investigated by Sullivan, *Z. physikal. Chem.*, 1899, **28**, 523.

energy would be too low. Since the results are reproducible even at high temperatures, it seems that saturation is, in fact, maintained.

The values for the solubility are given in Table III. At least two experiments were made at each temperature, and a mean taken. The results are considered accurate to within 10%

TABLE I.

Course of the reaction at 111·3°.

Time (mins.).	x/a.	$\dfrac{2\cdot303 \log_{10} x/a}{t - 3\cdot00}$.	Time (mins.).	x/a.	$\dfrac{2\cdot303 \log_{10} x/a}{t - 3\cdot00}$.	Time (mins.).	x/a.	$\dfrac{2\cdot303 \log_{10} x/a}{t - 3\cdot00}$.
61	0·055	1·47	131	0·312	1·42	163	0·680	1·37
81	0·100	1·40	145	0·416	1·51	175	0·886	1·47
111	0·172	1·54	154	0·564	1·33	176	0·910	1·41

TABLE II.

Temp.	t' (hrs.).	$k_2 s$.	$\log_{10} k_2 s$.	$\log_{10} k_1$.	Temp.	t' (hrs.).	$k_2 s$.	$\log_{10} k_2 s$.	$\log_{10} k_1$.
120·2°	1·15	4·57	0·660	$\bar{2}\cdot38$	90·9°	31·0	0·118	$\bar{1}\cdot072$	$\bar{3}\cdot48$
111·3	3·00	1·44	0·158	$\bar{2}\cdot28$	80·6	116	0·0291	$\bar{2}\cdot464$	$\bar{3}\cdot00$
100·6	10·00	0·384	$\bar{1}\cdot584$	$\bar{3}\cdot92$					

TABLE III.

Temp.	95°	75°	55°	25°	0°
Solubility(s), g./g. $\times 10^4$	3·34	1·65	0·925	0·290	0·106

except at 0°. When log s is plotted against $1/T$, the results lie on a straight line, from which the negative heat of solution (Q) is found to be 7380 $\pm$ 300 cals. From the plot of log $k_2 s$ against $1/T$, $E_2 + Q = 34,400$ cals., where E_2 is the activation energy of the reaction in solution; therefore $E_2 = 34,400 - 7380 = 27,020$ cals. The activation energy for the solid reaction is 26,300 cals.

DISCUSSION.

The decomposition of iodonium salts may be compared with that of ammonium, phosphonium, and sulphonium salts: the chemical nature of these changes has been discussed by Hughes, Ingold, and Patel (J., 1933, 526). Kinetic measurements of the decomposition of a quaternary ammonium iodide in aqueous solution indicate that the reaction is unimolecular (Hughes and Ingold, *ibid.*, p. 523). An extensive investigation of the decomposition of phenylbenzylallylammonium bromide in various solvents has been made by von Halban (*Ber.*, 1908, **41**, 2417). In each solvent the reaction is unimolecular. The observed rate has been compared (Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1933, p. 158 *et seq.*) with that calculated from the formula

$$k = (3\pi\eta\sigma/2m) \, . \, e^{-E'/RT} \, . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

based upon a rough value for the number of collisions between solvent and solute with activation energy E' in two square terms; E' is the observed activation energy corrected for the temperature variation of the solute–solvent collision number. In chloroform solution the observed rate is about 10^5 times greater than that given by (3). Similarly, the observed rate of decomposition of triethylsulphonium bromide (von Halban, *Z. physikal. Chem.*, 1909, **67**, 129) in various solvents is about 10^5 times as great as that given by the equation. These observed rates can naturally be explained if the energy of activation is distributed in a number of degrees of freedom, the minimum number required being about 7 in some examples.

The method by which the decomposition of diphenyliodonium iodide has been studied does not give the order of the reaction, as the concentration remains constant, but the change is probably unimolecular, as in the other examples. This being assumed, calculations similar to those described above may be carried out. The activation energy (E_2) must be increased by Q' of the equation $-d \log_e \eta/dT = Q'/RT^2$, where η is the viscosity of iodobenzene; $Q' = 2480$ cals. (Intl. Crit. Tables), so $E' = 27,020 + 2480 = 29,500$ cals. If $\sigma = 5 \times 10^{-8}$ cm., the value of the right-hand side of (3) at 90·9° is of the order 10^{-5} to 10^{-6} sec.$^{-1}$. The observed value of $k_2 s$ at 90·9° is 0·118 hr.$^{-1}$ or $3\cdot28 \times 10^{-5}$ sec.$^{-1}$. From the graph of log s against $1/T$, s at 90·9° is $2\cdot83 \times 10^{-4}$; therefore $k_2 = 0\cdot116$. The

observed rate is thus 10^4—10^5 times as great as that calculated from equation (3), this ratio being comparable with that found with ammonium and sulphonium salts. The observed rate of reaction is many powers of ten greater than that calculated for a bimolecular reaction between two molecules of the solute, or between a diphenyliodonium ion and an iodide ion. It seems probable, therefore, that the assumption of a unimolecular reaction is justified.

The Reaction of the Solid.—Many solid reactions take place only at an interface between the reacting substance and one of the products. Widely differing types of behaviour are found, but in certain examples, such as the dehydration of copper sulphate pentahydrate (Topley, *Proc. Roy. Soc.*, 1932, *A*, **136**, 413), the rate of reaction and its variation with temperature have been accounted for satisfactorily.

From the nature of the experimental method, only the initial stage of the decomposition of solid diphenyliodonium iodide contributes towards the velocity constant, k_1. The course of reaction to be expected·if decomposition occurs only at an interface will not therefore be apparent.

The velocity constant (k_1 in sec.$^{-1}$) is given by $k_1 = 6 \cdot 0 \times 10^9 \cdot e^{-26,300/RT}$. It is of interest to see the result of assuming that the reaction may take place uniformly throughout the whole mass of solid. If the energy of activation is contained in two square terms, $6 \cdot 0 \times 10^9$ is the probability of decomposition of the activated molecules, and the reciprocal of this is the average life of an activated molecule. If the energy of activation is distributed throughout the molecule in a number of degrees of freedom, and the probability of decomposition represents the chance that sufficient energy becomes localised in a certain part of the molecule (*e.g.*, the C–I bond), then the expression $e^{-26,300/RT}$ must be replaced by a more complex one. If all the C–C and C–I bonds were involved, the number of square terms could be very great, and the average life might work out to be as great as 10^{-4} sec. This state of affairs would be comparable with that met with in the unimolecular decompositions of complex molecules in the gaseous state.

Further knowledge of the rate of reaction in other solvents seems necessary before more can be said about the mechanism of the change. Without definite knowledge of the number of degrees of freedom participating in the decomposition of the solid, and in the decomposition in solution, it is not permissible to compare the activation energies directly. If the number is the same in the two cases, the energy of activation in iodobenzene appears to be somewhat greater than that for the solid.

SUMMARY.

The rate of decomposition of diphenyliodonium iodide has been studied in the solid state and in solution in iodobenzene. The activation energy for the reaction in the solid is 26,300 cals., and that for the reaction in solution 27,000 cals. (uncorrected for change of viscosity). The solubility of diphenyliodonium iodide in iodobenzene has also been measured.

The rates of reaction are discussed in relation to different activation mechanisms.

132. *The Reaction of Hydrogen Chloride with Methyl Alcohol.*

By C. N. HINSHELWOOD.

SINCE in the formation of a carboxylic ester the hydroxyl group is detached from the acid (Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, **80**, 508), it must be the hydrogen atom and not the hydroxyl group which is detached from the alcohol. In the formation of an alkyl halide from the hydrogen halide and an alcohol, however, the hydroxyl must be

replaced by the halogen atom. Hence, there must be a rather important difference in mechanism between the two processes :

$$R \cdot CO|OH + RO|H = R \cdot CO_2R + H_2O \quad \text{and} \quad H|Cl + R|OH = RCl + H_2O.$$
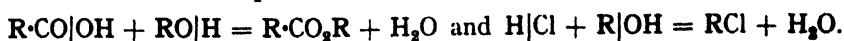
This difference is reflected in the different effects of substitution on the two types of reaction (Bennett and Reynolds, this vol., p. 131), tertiary alcohols reacting less rapidly than primary alcohols with acetic acid and more rapidly with hydrogen bromide.

It is the object of this paper to point out that kinetic observations also indicate a fundamental difference between the mechanisms concerned in the formation of alkyl halides and in that of carboxylic esters.

The interaction of hydrogen chloride with ethyl and with propyl alcohol was investigated by Kilpi (*Z. physikal. Chem.*, 1929, *A*, **141**, 424; 1933, *A*, **166**, 285), who found complex relations between the rate of reaction and the concentrations of reactants, water, and added electrolytes. He concluded that the results could be interpreted by assuming that the rate varied as the product of the activities of chlorine ions and hydrogen ions.

In the course of investigations of the formation of carboxylic esters under the influence of hydrogen chloride as a catalyst, measurements have been made of the rate of interaction of methyl alcohol and hydrogen chloride. The method of measurement was to seal up solutions of hydrogen chloride in anhydrous methyl alcohol (prepared by the method of Hartley and Raikes, J., 1925, **127**, 524), and analyse them after they had been kept for a known time in a thermostat.
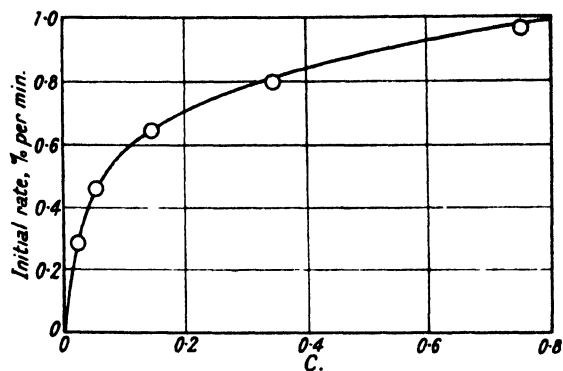
The reaction is retarded by the water formed : to eliminate this complication as far as possible, initial rates of reaction were found by drawing tangents to curves of percentage change against time. The values of the initial rate, *r*, expressed as percentage change per minute at 80·0°, are given below and plotted in the figure. The concentration, *c*, is the total acidity determined by titration, and expressed as a normality.

c	0·754	0·345	0·144	0·0553	0·0216
r	0·97	0·80	0·645	0·47	0·285

If we assume the only species present, apart from solvent, to be chlorine ions, methoxonium ions, and ion-pairs $MeOH_2^+ \cdot Cl^-$, then we have

$$c_{MeOH_2^+Cl^-} = c_{Cl^-} c_{MeOH_2^+} \; f_{Cl^-} f_{MeOH_2^+} / f_{MeOH_2^+Cl^-}$$

The rate of reaction may depend upon the rate of dehydration of the methoxonium chloride ion-pairs. The degree of ionisation is considerable. Therefore, if the activity coefficients were constant, the reaction would be bimolecular with respect to the total hydrogen chloride, and the curve in the figure would be a straight line passing through the origin and inclined at an angle to the axes. But the activity product on the right will diminish with increasing total ionic concentration; hence the rate will increase less rapidly than corresponds to a second-order reaction, which is qualitatively in accordance with the behaviour shown in the figure.

The temperature coefficient was determined for 0·0991*N*-solutions.

Temp.	100·0°	84·2°	80·0°	68·4°	56·3°	40·0°
Initial rate, % per min.	2·77	0·80	0·57	0·146	0·037	0·00419

These values give an energy of activation of 26,000 cals. This result is not sensitive to the influence of water, since from the times required for 25% and 50% reaction respectively, the values of *E* found are 26,900 and 27,000.

Experiments were also made with 0·426N-solutions of hydrogen chloride in *tert.*-butyl alcohol, and led to the result $E = 26,800$ cals.

These values are to be compared with that just published by Bennett and Reynolds (*loc. cit.*) for methyl alcohol and hydrogen bromide, *viz.*, 26,600 cals.

These high activation energies for the formation of alkyl halides are to be contrasted with the much smaller values found for the formation of carboxylic esters, *e.g.*, 10,200 for the esterification of acetic acid by methyl alcohol under the influence of the hydrion, and 13,000 for the same reaction catalysed by the undissociated molecules of acetic acid itself.

The differences appear to be out of all proportion to the differences in the rates, and themselves indicate a fundamentally different mechanism for the two types of reaction.

The esterification of a carboxylic acid demands the presence of acid, alcohol, and acid catalyst, and if interpreted as a termolecular interaction of these compounds it can be shown to be very much slower than the possible rate of activation (Rolfe and Hinshelwood, *Trans. Faraday Soc.*, 1934, **80**, 935). It will now be of interest to examine the hypothesis that the formation of alkyl halides depends upon the dehydration of the alkoxonium chloride ion-pairs. If this is the mechanism, the observed activation energy must be corrected for the variation of ion-pairs with temperature. This depends upon the differences between much larger thermal quantities measuring the interaction of ions and solvent and may be positive or negative. In view of the closeness of the values of E for methyl and *tert.*-butyl alcohol, and for hydrogen chloride and hydrogen bromide, we will risk the assumption that the correction is not large, and that it certainly will not reduce the value 26,000—27,000 cals., characteristic of the halide formation, to anything like the value 10,000—15,000 characteristic of carboxylic ester formation.

We may reach certain qualitative, but interesting, conclusions about the molecular statistics of the reaction in the following way, using the results recorded above for the formation of methyl chloride. At 80·0° for $N/2$-solution, $-(100/c) \cdot dc/dt = 0\cdot865$ min.$^{-1}$ $= 1\cdot44 \times 10^{-2}$ sec.$^{-1}$, whence $(1/c) \cdot dc/dt = 1\cdot44 \times 10^{-4}$. This would be the unimolecular velocity constant for the decomposition of the methoxonium chloride if all the hydrogen chloride present were in that form. Since only a fraction is actually present in the form of undissociated ion-pairs, we are safe in assuming that the unimolecular velocity constant for the actual decomposition of the ion-pairs is not less than this value. We conclude, then, that k is greater than 10^{-4} sec.$^{-1}$, and probably very considerably greater.

Activation of the ion-pairs presumably occurs by collision with solvent molecules. Applying the formula $k = (3\pi\sigma\eta/2m)e^{-E/RT}$ (see preceding paper), and adding to 26,000 the viscosity correction for methyl alcohol, *viz.*, 2500 cals., making $E = 28,500$ cals., we find for 80°, $k = 2 \times 10^{-5}$. Thus the observed value must be considerably greater than that given by the formula. That this formula can give more than the crudest idea of the rate of activation by collision with solvent molecules is improbable. But the fact worthy of attention is that the result is similar to that found by applying the same formula to the decomposition of iodonium, sulphonium, and ammonium salts (see preceding paper), where the introduction of internal degrees of freedom is necessary to account for the rate. Thus, whatever the limitations of the method of calculation, it serves to indicate the probable analogy between the decomposition of the alkoxonium salt and that of the other " onium " salts. Moreover, the formula is probably exact enough at least to show that the reactions in question are not " slow " reactions in the same way as the esterification of the carboxylic acids.

<p style="text-align:center">SUMMARY.</p>

Kinetic considerations confirm the conclusions of organic chemical theory that the interaction of hydrogen halides and the simple alcohols differs in mechanism from the esterification of carboxylic acids. Experimental data for the reaction between methyl alcohol and hydrogen chloride are recorded.

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133. *Studies in Dielectric Polarisation. Part XII. Dipole Moments and Structure of Thiopyrones and Related Compounds.*

By F. ARNDT, G. T. O. MARTIN, and J. R. PARTINGTON.

IN Part V (J., 1933, 87) the dipole moments of some pyrone compounds were recorded. The present part describes the moments of the compounds (I)—(IV). The highly purified

| (I.) 2 : 6-Diphenylthio- | (II.) 2 : 6-Diphenyl- | (III.) 2 : 6-Diphenylthio- | (IV.) 2 : 6-Diphenylthio- |
| pyran-4-one. | thiopyrone. | pyran-4-one 1-dioxide. | pyrone 1-dioxide. |
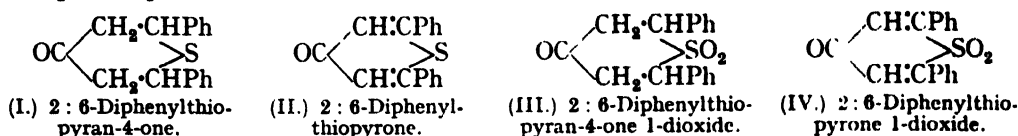
specimens used for the measurements were prepared as described by Arndt and co-workers (*Ber.*, 1925, **58**, 1633), except that the bromination of (III) was carried out in warm glacial acetic acid solution instead of chloroform, from which there is a tendency for the mono-brominated derivative to separate. [For the *cis*- and *trans*-forms of (I), cf. *Ber.*, 1930, **68**, 313.]

These compounds are of interest from the point of view of dipole-moment measurement in relation to the constitution of pyrones, which has been discussed for many years. A summary of the earlier literature on these compounds is given in Part V (*loc. cit.*), where values for the dipole moments of 2 : 6-dimethylpyrone, 2 : 6-diphenylpyrone, and 2 : 6-dimethyl-4-thiopyrone are given.

EXPERIMENTAL.

The apparatus used for dielectric-constant measurements, which was designed in collaboration with Mr. E G. Cowley, was a modification of that described previously (J., 1932, 2812). The heterodyne-beat method is employed, a valve-maintained quartz crystal being used for one of the oscillators. The second oscillator was tuned by a Muirhead standard variable air condenser of 150 $\mu\mu$F capacity, which could be increased by connecting a fixed air condenser of 100 $\mu\mu$F capacity in parallel with it. Both condensers had National Physical Laboratory calibrations accurate to 2 parts in 10,000, and, by means of the worm drive with which it was fitted, the variable condenser could easily be read to 1 part in 10,000. The lead-covered cable which was previously used for the leads to the variable condenser was replaced by a copper rod supported by bakelite bushes inside a stout copper tube, this tube forming the earthed conductor.

The dielectric cell was of the type described by Henriquez (*Physica*, 1933, **1**, 41), modified so that it could also serve as a pyknometer. Its capacity was 40 $\mu\mu$F, and weight about 55 g., 15 c.c. of solution being required to fill it.

The benzene used for the solutions was purified in the usual manner (see Part VIII, J., 1933, 1252).

Results.—The electronic polarisations P_E of the compounds were calculated (as in Part V) from the sum of the atomic refractions. The moments were calculated as in the previous papers of this series. All moments are given in Debye units (10^{-18} c.s.u.).

2 . 6-Diphenylthiopyran-4-one

cis-Form, m. p. 113°.					trans-Form, m. p. 87 .				
f_2.	$d_4^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.	f_2.	$d_4^{20°}$.	ϵ.	P_{12}, c.c.	P_2, c.c.
0·00000	0·8788	2·277	26·55	—	0·00000	0·8788	2·277	26·55	—
0·00933	0·8873	2·320	27·51	129·0	0·01118	0·8877	2·330	27·75	133·5
0·01248	0·8893	2·332	27·82	127·9	0·01537	0·8907	2·348	28·18	132·8
0·01536	0·8916	2·342	28·07	125·4	0·01967	0·8945	2·367	28·63	132·2
0·01847	0·8941	2·352	28·35	124·1	0·02519	0·8984	2·389	29·19	131·3

$P_{2\infty} = 135·6$ c.c.; $P_E = 78·8$ c.c.; $\mu = 1·64$ *D.* $P_{2\infty} = 135·35$ c.c.; $P_E = 78·8$ c.c.; $\mu = 1·62$ *D.*

2 : 6-*Diphenylthiopyrone*, m. p. 132°.					2 : 6-*Diphenylthiopyrone* 1-*dioxide*, m. p. 144°.				
0·00000	0·8788	2·277	26·55	—	0·00000	0·8782	2·274	26·51	—
0·00954	0·8872	2·554	30·71	462·5	0·01663	0·8960	2·328	27·98	114·85
0·01371	0·8911	2·666	32·31	446·2	0·01930	0·8987	2·336	28·21	114·76
0·02028	0·8969	2·847	34·77	431·6	0·02390	0·9036	2·351	28·61	114·70
0·02257	0·8987	2·910	35·61	427·7					

$P_{2\infty} = 486$ c.c.; $P_E = 78·4$ c.c.; $\mu = 4·39$ *D.* $P_{2\infty} = 115·2$ c.c.; $P_E = 86·3$ c.c.; $\mu = 0·93$ *D.*

DISCUSSION OF RESULTS.

For 2 : 6-diphenylthiopyrone (II), the calculated moment based on the formula (II), any interaction through the double bonds being neglected, is the difference between the moments of the $\underset{C}{\overset{C}{\diagdown}}C{=}O$ and the $\underset{C}{\overset{C}{\diagdown}}S$ group. The moments of benzophenone (3·0 *D*) and of diphenyl sulphide (1·5 *D*) being taken for these, the calculated moment is about 1·5 *D*, whereas the observed value is 4·4 *D*. Considerable interaction through the double bonds is thus indicated. In (I) the absence of the double bonds excludes the possibility of rearrangement occurring. From the difference between the moments of acetone (2·75 *D*) and of diethyl sulphide (1·57 *D*), the calculated moment is 1·18 *D*. Since this saturated ring is probably flexible, this can be considered to be in agreement with the value 1·6 *D* observed for both the *cis*- and the *trans*-form.

For (IV) the moment is calculated by taking the difference between those of the $\underset{C}{\overset{C}{\diagdown}}C{=}O$ and the $\underset{C}{\overset{C}{\diagdown}}S{\overset{O}{\underset{O}{\diagup}}}$ group. If the moments of benzophenone (3·0 *D*) and diphenylsulphone (5·1 *D*), respectively, are taken for these, the calculated moment is 2·1 *D*, while the value observed is 0·93 *D*. Obviously, this compound behaves in an entirely different manner from (II). Rearrangement of the double bonds cannot occur, since the lone pairs of electrons of the sulphur atom are no longer present, having been donated to the two oxygen atoms in the formation of the sulphone group. No electronic drift round the ring can take place, and the tendency for the two ends of the ring to become oppositely charged is no longer present. It need hardly be said that the migration of complete electrons in (II) is not permissible, since the molecule thus formed would have a very large moment (about 20 *D*), and such a migration has never been assumed either in this series of papers or in the earlier papers of one of the authors (Arndt, *Ber.*, 1924, **57**, 1906; 1930, **63**, 2963). The latter considered the actual state of the molecules of γ-pyrones and thiopyrones as lying " in between " the two states expressed by the unsaturated ketonic and the betainic formula, such " intermediate state " being interpreted as the time-integral of a very rapid electronic oscillation between the two states, the state corresponding to formula (II) being predominant. A similar view has recently been expressed by Sutton (Faraday Society Discussion on Dipole Moments, 1934), who explains the fact that pyrones do not possess such a large moment as complete ionisation would indicate, by assuming

(V.)   (VI.)

resonance between the two forms (V) and (VI), the first structure being the more important; a similar explanation for the thiopyrones is offered.

The dipole moment of 2 : 6-diphenylthiopyrone 1-dioxide (IV) is lower than the calculated value. This may perhaps be due to some effect of the double bonds, which is present in the case of thiophen (μ = 0·63 *D*; Hassel and Naeshagen, *Tids. Kjemi*, 1930, **10**, 81), the moment of which is much lower than that of an aliphatic sulphide, *e.g.*, diethyl sulphide (μ = 1·57 *D*; Part I, J., 1931, 2062). Another example of this effect is provided by furan (μ = 0·63 *D*; Part I, *loc. cit.*), the moment of which is also much smaller than that of an aliphatic ether, *e.g.*, diethyl ether (μ = 1·22 *D*; Krchma and Williams, *J. Amer. Chem. Soc.*, 1927, **49**, 2408). These low values cannot be completely explained by widening of the valency angle, since this assumption (Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230) leads to improbably large values for the valency angles.

The solubility of 2 : 6-diphenylthiopyran-4-one 1-dioxide (*cis*-form) (III) in benzene at 20° was too small to allow of a measurement being taken. The only suitable solvent found was dioxan, and measurements then indicated a large moment (about 3 *D*), but it appeared that some action between the compound and the solvent can occur. The solution on keeping changed from colourless to pale yellow, and later deposited a slight brownish-purple precipitate, the amount of which had become appreciable after 2 or 3 days. Distil-

lation of the dioxan under reduced pressure (2—3 cm.) left a yellowish residue, but on re-fluxing with benzene the colour practically disappeared, and the compound crystallised perfectly colourless and with an m. p. identical with that of the original specimen. A small quantity of yellow substance remained on the sides of the dish, and the m. p. of the last portion recovered was depressed.

Although no definite significance can be attached to the measurements in dioxan solution, the compound (III) might, by calculation, be expected to have a moment of about 2 *D*, *i.e.*, greater than that observed for the compound (IV).

Further information is provided by measurements of the heats of combustion of these compounds (Lorenz and Sternitzke, *Z. Elektrochem.*, 1934, **40**, 501). Details of these experiments are to be published elsewhere, and we have to thank Dr. Lorenz for permission to reproduce the following data for the molecular heats of combustion (all in kg.-cals.) :

				Diff.
(I)	$2268 \cdot 6 \pm 2 \cdot 31$	(II)	$2165 \cdot 5 \pm 2 \cdot 77$	$103 \cdot 1$
(III)	$2188 \cdot 6 \pm 2 \cdot 85$	(IV)	$2118 \cdot 2 \pm 2 \cdot 34$	$70 \cdot 4$
Diff.	$80 \cdot 0$		$47 \cdot 3$	$32 \cdot 7$

The difference between the constitutions of (III) and (IV) is the same as between 2 mols. of ethane and 2 mols. of ethylene. The difference between their molecular heats of combustion is 70·4 kg.-cals., which is in good agreement with that between the heats of combustion of 2 mols. of ethane and 2 mols. of ethylene, which, according to Thomsen, is 74·2 kg.-cals. The difference between the heats of combustion of (I) and (II), however, is 103·1 kg.-cals.; 2 : 6-diphenylthiopyrone (II) therefore contains less energy than that required by an exact conformity with formula (II). This deficit of 32·7 kg.-cals. is the " energy of aromatisation " of the pyronic nucleus. By considering the problem from another angle, it is seen that the difference between the heats of combustion of (I) and (III) is 80·0 kg.-cals. This difference is the heat of " combustion " of S to SO_2 within the molecule. The difference between the heats of combustion of (II) and (IV) is only 47·3 kg.-cals. This means that on oxidation of the sulphur atom in the thiopyrone (II) to the sulphone group in (IV), 32·7 kg.-cals. of the 80·0 kg.-cals. gained by the oxidation are used up in destroying the cyclic conjugation in (II) which is no longer present in (IV).

SUMMARY.

The dipole moments of 2 : 6-diphenylthiopyrone, 2 : 6-diphenylthiopyran-4-one, and their dioxides have been measured, and the results discussed in relation to their heats of combustion. The conclusions previously reached by one of the authors (Arndt) regarding the constitution of these compounds have been confirmed.

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134. *Studies in Dielectric Polarisation. Part XIII. The Dipole Moments of the Simpler Aliphatic Nitriles.*

By ERIC G. COWLEY and JAMES R. PARTINGTON.

SEVERAL determinations of the dipole moments of the simpler aliphatic nitriles have previously been made, but the results obtained are somewhat widely divergent as is seen from Table I. (In all cases the solvent used was benzene.) From these data it is difficult to reach a decision on the important question as to whether the nitriles have a constant moment, which is independent of the length of the hydrocarbon chain, or whether the moment becomes larger with increasing length of the chain. On the whole, the latter view seems to be supported, although the individual values differ markedly. We have

TABLE I.

μ, in D units.

	Temp.	25°.	20°.	18°.	20°.	25°.	(Vapour.)
Acetonitrile		3·4 [1]	3·11 [2]	3·51 [3]	3·16 [4]	3·45 [5]	3·94 [6]
Propionitrile		3·4 [1]	3·34 [2]	3·66 [3]	—	—	4·05 [6]
n-Butyronitrile		--	3·46 [3]	—	—	—	—

[1] Williams, *Z. physikal. Chem.*, 1928, **133**, 75.   [2] Werner, *ibid.*, 1929, B, **4**, 371.   [3] Eide and Hassel, *Tids. Kjemi,* 1930, **10**, 63.   [4] Hunter and Partington, J., 1932, 2812.   [5] Snoek, *Physikal. Z.*, 1934, **35**, 196.   [6] Højendahl, Thesis, Copenhagen, 1928 : values calculated from the data of Pohrt, *Ann. Physik,* 1913, **42**, 569.

therefore re-investigated the moments of pure specimens of four simple aliphatic nitriles and find that the dipole moment measured in benzene increases from aceto- to propionitrile, but then preserves a constant value in the higher members of the series, *viz.*, n-butyro- and n-valero-nitrile. The significance of this result is discussed on p. 608.

EXPERIMENTAL.

Dielectric Constants.—The electrical circuit, which is based on the heterodyne method, as previously used by us (J., 1933, 1252) and described by Hunter and Partington (J., 1932, 2812), has been improved in several respects. The two oscillators are contained in earthed copper boxes, and loosely coupled to the detector-amplifier; they are described in Part XII (preceding paper). The true capacities of the condensers are obtained correct to 0·02 $\mu\mu$F by translating the scale readings by means of large-scale calibration charts. The leads were as already described (*loc. cit.*). The sources of high and low tension are batteries of 120 volts, and three 2-volt accumulators, respectively, and these batteries are switched on about an hour before measurements are commenced. The zero point on the standard condenser is then quite steady, and the silent point is very sharp.

Dielectric Cell.—The dielectric cell consisted of a glass vessel, inside which the condenser plates of polished nickel were supported by nickel rods from the bakelite stopper, which was accurately ground to fit the glass vessel. Connexion to the standard condenser was made by a small bridge of stout copper wires, held rigidly apart, linking the small mercury cups on both the cell and the leads. The cell itself was immersed in a small, earthed, copper oil-bath, supported firmly on a ring of bakelite, which fitted a ground joint on the bottom of the glass container. The oil-bath was held in position in a large water thermostat, controlled at 20·0° $\pm$ 0·05°. The correction due to the leads was found by determining the capacity of the cell when filled with pure liquids of known dielectric constant. The electrical capacity of the cell was 52 $\mu\mu$F, and its volume 12 c.c.

Refractivities and Densities.—The refractivities were determined with a Pulfrich refractometer, and the densities by a 10-c.c. pyknometer. All measurements were made at 20·0° $\pm$ 0·05°. The refractive indices are correct to 0·0001, and the error on the densities is less than 0·0001.

Calculation of the Dipole Moment.—The symbols and method of calculation are the same as in previous parts of this series and, as before, the atomic polarisation is left undetermined. All electric moments are expressed in Debye units of 10^{-18} e.s.u.

Accuracy.—The dielectric constant of benzene is correct to $\pm$ 0·001 and those of solutions are correct to within 0·08%. The error on the polarisations of the solutes, $P_{2\infty}$, is not greater than 1·5 c.c., and the experimental errors on the electric moments are less than $\pm$ 0·02 D.

Preparation of Materials.—*Nitriles.* All the nitriles were purchased from Kahlbaum, with the exception of n-butyronitrile, which was supplied by Schuchardt. They were purified by standing over solid caustic potash for 2 days, to remove any acid formed by slight hydrolysis, then left in contact with calcium chloride for a week, to remove any ammonia, and finally dried by phosphoric oxide, over which they were twice fractionated. We have suggested (*Nature,* 1935, **135**, 474) that the previously recorded low values for acetonitrile may be, in part, due to the method of purification used, since repeated fractionation with phosphoric oxide would not remove traces of acetic acid, which has a dipole moment of about 0·8 D (Wolf, *Physikal. Z.,* 1930, **31**, 227). It is, however, very difficult to assess the purity of the materials used in previous work, since the observers have not recorded either the density or the refractive index of their specimens. The physical constants of the materials used in the present research are given in Table II.

TABLE II.

Compound.	B. p.	$D_4^{20°}$.	$n_D^{20°}$.	$[R_L]$.
Acetonitrile	81·6°/760 mm.	0·7823	1·3438	11·12
Propionitrile	96·8/743	0·7830	1·3664	15·76
n-Butyronitrile	116·8/742	0·7911	1·3839	20·42
n-Valeronitrile	140·4/741	0·8014	1·3982	25·03

The following figures are available for comparison :

Acetonitrile : b.p. 81·7°/761·5 mm. ; $D_4^{20°}$ 0·7825 ; $n_D^{20°}$ 1·3439 (Lowry and Henderson, *Proc. Rov. Soc.*, 1932, *A*, **136**, 471) ; $D_4^{20°}$ 0·7823 (I.C.T.). Propionitrile : b. p. 97·0°/752·5 mm., $D_4^{20°}$ 0·7827, $n_D^{20°}$ 1·3661 (*idem, ibid.*) ; $D_4^{20°}$ 0·783 (Walden, *Z. physikal. Chem.*, 1910, **70**, 575) ; b. p. 95·0°/722 mm. (Timmermans, *Proc. Roy. Dublin Soc.*, 1912, **13**, 310). *n*-Butyronitrile : b. p. 115·4°/739 mm. (*idem, ibid.*) ; $D_4^{20°}$ 0·7909, $n_D^{20°}$ 1·383 (I.C.T.) ; $D_4^{20°}$ 0·7904 (Hawkins, Clark, and Roberts, *J. Amer. Chem. Soc.*, 1920, **42**, 705). *n*-Valeronitrile : b. p. 141·7—142°/763 mm., $D_4^{20°}$ 0·7949 (Kilpi, *Z. physikal. Chem.*, 1913, **86**, 671) ; $D_4^{20°}$ 0·801, $n_D^{20°}$ 1·3909 (I.C.T.) ; $D_4^{20°}$ 0·7935 (Morgan and Chazal, *J. Amer. Chem. Soc.*, 1913, **35**, 1821).

Benzene. The benzene used as solvent was Kahlbaum's " thiophen-free " material. It was dried over sodium and carefully fractionated. Kahlbaum's benzene " for analysis and molecular-weight determination " was subjected to the same treatment and used for calibrating the dielectric cell.

Results.—The solvent throughout is benzene, and all the measurements are at 20°.

f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.	f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.
		Acetonitrile.					*Propionitrile.*		
0	2·280	0·8788	26·57	—	0	2·281	0·8789	26·58	—
0·00896	2·430	0·8782	28·58	250·6	0·00602	2·389	0·8784	28·08	275·8
0·01410	2·518	0·8780	29·68	247·0	0·00844	2·430	0·8782	28·63	269·5
0·01877	2·592	0·8777	30·56	239·4	0·01118	2·477	0·8781	29·24	264·5
0·02749	2·735	0·8774	32·18	230·6	0·01917	2·616	0·8775	30·97	255·6
0·03122	2·798	0·8773	32·86	227·9	0·02654	2·741	0·8770	32·44	247·4
0·03295	2·827	0·8770	33·17	226·9	0·03697	2·915	0·8764	34·33	236·2
0·04661	3·054	0·8763	35·41	216·2	0·04741	3·096	0·8756	36·16	228·6

$P_{2∞} = 262$ c.c. ; $P_E = 11·1$ c.c. ; $P_{2∞} = 285$ c.c. ; $P_E = 15·8$ c.c. ;
$P_{2∞} - P_E = 250·9$ c.c., $\mu = 3·44$ D. $P_{2∞} - P_E = 269·2$ c.c. ; $\mu = 3·57$ D.

f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.	f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.
		n-*Butyronitrile*					n-*Valeronitrile.*		
0	2·281	0·8789	26·58	—	0	2·281	0·8789	26·58	—
0·00757	2·417	0·8782	28·50	280·2	0·00670	2·400	0·8781	28·30	283·3
0·01131	2·486	0·8778	29·42	277·7	0·00958	2·452	0·8779	29·02	281·3
0·01651	2·578	0·8774	30·61	270·8	0·01362	2·522	0·8775	29·97	275·5
0·02183	2·675	0·8771	31·81	266·2	0·01881	2·611	0·8771	31·14	269·0
0·02729	2·770	0·8766	32·95	260·0	0·02654	2·746	0·8764	32·83	262·1
0·03653	2·935	0·8758	34·81	251·9	0·03924	2·969	0·8753	35·43	252·1
0·04562	3·101	0·8752	36·55	245·1	0·04630	3·095	0·8747	36·81	247·5

$P_{2∞} = 290$ c.c. ; $P_E = 20·4$ c.c., $P_{2∞} = 295$ c.c. ; $P_E = 25·0$ c.c. ;
$P_{2∞} - P_E = 269·6$ c.c., $\mu = 3·57$ D. $P_{2∞} - P_E = 270·0$ c.c. ; $\mu = 3·57$ D.

DISCUSSION OF RESULTS.

The following values of μ have been obtained :

| Acetonitrile | 3·44 D | *n*-Butyronitrile | 3·57 D |
| Propionitrile | 3·57 D | *n*-Valeronitrile | 3·57 D |

It has already been pointed out (*Nature*, 1935, **135**, 474) that the present value for aceto-nitrile is in excellent agreement with that of Snoek (*loc. cit.*), viz., 3·45 D, as found from measurements in benzene, hexane, and carbon tetrachloride. It appears, however, that the existing values for propionitrile and *n*-butyronitrile are incorrect (see Table I). The moment of *n*-valeronitrile has been determined for the first time. The indications of the present results are given on p. 608.

With the exception of Williams's values (*loc. cit.*), which are probably to be regarded as superseded, all the previous determinations in solution, although they exhibit differ-ences amongst themselves, agree in making the moment of propionitrile higher than that of acetonitrile. This is supported by the approximate values for the vapours calculated by Højendahl (*loc. cit.*). Werner (*loc. cit.*) detected a regular variation of dielectric

constant, moment, and molar volume through the series of nitriles. In general, thére is no direct relationship between the dielectric constant of a substance and its moment, and the present values show that in the case of the cyanides, there is no proportionality between the molar volume and the moment.

The moments found for these nitriles may now be compared with those for other similar series of compounds. The simplest of these is that comprising the alkyl halides, for which accurate values of the moments are available. It is well established that there is a definite increase in moment from the hydrogen halide extending as far as the ethyl compound : this is illustrated in Table III. It is quite generally found that the moment

TABLE III.

| | Fluoride. | Chloride. | Bromide | Iodide. | Cyanide. | |
					Solution.	Vapour.
Hydrogen	--	1·02 [2]	0·78 [2]	0·38 [2]	2·65 [4]	2·93 [6]
Methyl	1·81 [1]	1·86 [3]	1·78 [1]	1·59 [1]	3·44 [5]	3·94 [7]
Ethyl	1·92 [1]	2·04 [3]	2·02 [1]	1·90 [1]	3·57 [5]	4·05 [7]
n-Propyl	—	2·04 [3]	—	—	3·57 [5]	—
n-Butyl	—	2·04 [1]	—	—	3·57 [5]	—

[1] Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499   [2] Zahn, *Physical Rev.*, 1926, **27**, 455.
[3] Sänger, *Physikal. Z*, 1931, **32**, 20; cf. Fuchs, *Z. Physik*, 1930, **63**, 824.   [4] Werner, *loc. cit.*
[5] Present research.   [6] Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1934, **56**, 1697   [7] Højendahl, *loc. cit.*

of a substance is higher in the vapour state than in solution. Hydrogen cyanide in the vapour state has a moment of 2·93 D, which is higher than the values found in solution by Werner (*loc. cit.*), 2·65 D, and by Lutgert (*Z. physikal. Chem.*, 1931, *B*, **14**, 27), 2·53 D. Smyth ("Dielectric Constant and Molecular Structure," 1931, 74) assumes that the principal dipole of the halides induces moments along the hydrocarbon chain, resulting in an increase of moment in the homologous series. The figures in Table III indicate, however, that this increase is detectable only as far as the ethyl compound.

Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1367), from considerations based on wave mechanics and a probable electronic structure of the molecule, concludes that the hydrogen cyanide molecule is linear, and a photographic investigation of the band spectra of the vapour in the near infra-red region (Badger and Binder, *Physical Rev.*, 1931, **37**, 800) confirms this result. Choi and Barker (*ibid.*, 1932, **42**, 777) and Brackett and Liddel (*Smith. Misc. Collect.*, 1931, **85**, No. 5) have also concluded, from the infra-red absorption spectrum of the acid, that the molecule is linear, and this configuration may be regarded as well established.

A consideration of the dipole moments of the aromatic nitriles also throws some light on this matter. If the C–CN group is straight, it would be expected that vector-addition rules would apply to p-substituted benzene compounds containing only groups the moments of which act in the direction of the carbon valencies of the benzene ring. The results for some of these compounds (cf. Hampson and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **140**, 562) are given below :

Compound.	μ, obs.	μ, calc.	Compound.	μ, obs.	μ, calc.
p-Toluonitrile	4·37	4·35	p-Bromobenzonitrile	2·64	2·38
p-Nitrobenzonitrile	0·69	0·03	p-Iodobenzonitrile	2·80	2·63
p-Chlorobenzonitrile	2·61	2·34			

The values (in D) are calculated from the following moments : $Ph\cdot NO_2$ 3·93, $Ph\cdot CN$ 3·90, $PhCl$ 1·56, $PhBr$ 1·52, PhI 1·27, and $Ph\cdot CH_3$ 0·45.

The differences between the calculated and the observed values in this table have been accounted for in several ways. They may be due to the fact that the linking of the nitrile group to the ring makes an angle with the line joining the carbon and nitrogen atoms (Bergmann and Tschudnowsky, *Z. physikal. Chem.*, 1932, *B*, **17**, 116) ; or to inductive effects caused by the strongly polar nitro- or nitrile groups (Poltz, Heil, and Strasser, *ibid.*, p. 155) ; or to the neglect of the atomic polarisation (Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 1854). It is noteworthy that the observed and the calculated

values do not agree for p-substituted benzene compounds containing groups which are supposed to give rise to large opposed electromeric effects (Hampson and Sutton, *loc. cit.*), and this may explain the discrepancy. Since the differences are in most cases quite small, it may be assumed that the nitrile group has a linear structure in these aromatic compounds as well as in the aliphatic series.

The alkyl cyanides will then be comparable with the alkyl halides and hydrogen cyanide with hydrogen chloride. It might be expected that the dipole moments of the two classes of compound would be analogous, and that induction effects would occur in both series. It may be noted that the conclusion reached by Hunter and Partington (J., 1932, 2825), that the *iso*thiocyanate group has an extended structure, has been confirmed from a study of the Raman spectra of the compounds (Langseth, Nielsen, and Sorenson, *Z. physikal. Chem.*, 1934, *B*, **27**, 101). In this series, dipole induction effects occur. The large moment of hydrogen cyanide must be due to unequal sharing of the six electrons forming the three covalent links between the carbon and the nitrogen nuclei, H:C:::N:, the nitrogen atom being negative with respect to the carbon, since the moment of the nitrile group in aromatic compounds acts in the same sense as that of the nitro-group, *i.e.*, away from the ring (cf. Sidgwick, "The Covalent Link in Chemistry," 1933, 151).

The relative increase caused by induction in the nitriles is smaller than that in the case of the halides, in spite of the greater magnitude of the nitrile dipole. This is shown by the data in Table III. The increase from Smyth and McAlpine's value, 2·93 D, for hydrogen cyanide vapour, which is more accurate than earlier results, to the figure 3·94, calculated by Højendahl for acetonitrile vapour, is probably too large, since the latter value can only be regarded as approximate. It is evident that the induced moments in the nitriles are of the same order as in the chlorides, and that the induction extends as far as the ethyl compound in both series, although the dipole in the former is much larger. Smyth and McAlpine (*J. Chem. Physics*, 1934, **2**, 499) have shown that there are qualitative analogies and differences between the Raman frequencies and the dipole moments of the alkyl halides. The frequency, which probably corresponds to a longitudinal vibration in the carbon–halogen line, falls from the methyl to the ethyl compound and then remains constant as the hydrocarbon chain is lengthened. The decrease in frequency corresponds with an increase in moment. The figures for the n-chlorides and cyanides (Kohlrausch, "Der Smekal–Raman Effekt," 1931, 304) are given below :

Compound.	Raman frequency, $\Delta\nu$, cm.$^{-1}$.		Compound.	Raman frequency, $\Delta\nu$, cm.$^{-1}$.	
	Chloride.	Cyanide.		Chloride.	Cyanide.
Methyl	712	2250	n-Propyl	651	2245
Ethyl	655	2246	n-Butyl	650	2245 (iso-)

It will be seen that, in the nitrile series, the Raman frequency also falls from the methyl to the ethyl member and then becomes constant, although the change in this case is much smaller.

Smyth and Walls (*loc. cit.*) have attributed the larger difference between the moments of phenylacetonitrile and acetonitrile, as compared with that between the corresponding halides, to an inductive effect, but if we take the new value for acetonitrile, the differences are seen to be of the same order for all the compounds. This result supports the assumption that the inductive action of the nitrile group is no greater than that of halogens. It might be expected that the influence of the larger cyanide dipole would extend further along the chain, as is indicated by Werner's earlier results (*loc. cit.*), but when the locations of the dipoles are considered, it is evident that such an extension is improbable. Smyth and McAlpine (*J. Chem. Physics*, 1933, **1**, 190), on the assumption that the C–Cl dipole is located $\frac{3}{4}$ of the distance from the carbon to the chlorine nucleus (cf. Meyer, *Z. physikal. Chem.*, 1930, *B*, **8**, 190), have calculated moments for the halogenated methanes which are in good agreement with experimental values. The principal dipole in the hydrogen cyanide molecule is situated between the carbon and the nitrogen nucleus, although its exact position is unknown. Badger and Binder (*loc. cit.*) calculate the value $18·79 \times 10^{-40}$ g. cm.^{2} for the moment of inertia of the hydrogen cyanide mole-

cule, and hence the C–N distance is found to be 1·15 Å.U. Mecke ("Structure of Molecules," ed. P. Debye, 1932, 30) gives the C–H distance as 1·08 Å.U. Meyer (*loc. cit.*) takes the C–Cl distance as 1·85 Å.U., and the C–C distance 1·55 Å.U. The position of the main dipole in methyl chloride is situated $\frac{1}{2} \times 1.76 = 1.54$ Å.U. from the carbon. The location of the principal dipole in hydrogen cyanide may be assumed, from a consideration of the centres of gravity of the charges, to be approximately mid-way between the carbon and the nitrogen nucleus. The distance of this dipole from the methyl carbon in aceto-nitrile is $\frac{1}{2} \times 1.15 + 1.55 = 2.13$ Å.U. Thus, although the magnitude of the principal dipole is greater in the nitriles than in the chlorides, the greater distance of the location of the dipole from the chain compensates for this, with the result that the induced moments are no larger in the first case than in the second.

SUMMARY.

The dipole moments of aceto-, propio-, *n*-butyro-, and *n*-valero-nitriles have been measured, and it has been shown that the moment increases in the series as far as propio-nitrile. Beyond this, the moments are constant. These results are discussed with reference to the alkyl halides and other nitriles.

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135. *The Electrical Polarisation of Concentrated Solutions of Nitrobenzene, with Special Reference to the Validity of the Sugden Relation.*

By H. O. JENKINS and L. E. SUTTON.

THE electrical polarisations of nitrobenzene solutions are of interest for several reasons. Davy and Sidgwick (J., 1933, 282) showed that, for benzene solutions of nitrobenzene, degrees of association calculated from cryoscopic measurements are in approximate agreement with those obtained from electrical polarisations. However, marked disagreement results for *cyclo*hexane solutions of nitrobenzene, if it is assumed that the polarisation–concentration curve is of normal type, since abnormally high degrees of association are obtained from the freezing-point measurements. The form of the polarisation–concentration curve has therefore been determined and compared with those in other solvents.

Curves in benzene, carbon disulphide, *n*-hexane, and carbon tetrachloride have been studied in addition, in order to test the empirical relation formulated by Sugden (*Nature*, 1934, **133**, 415) and used by Fairbrother (*ibid.*, **134**, 458; J., 1934, 1946) and, in a different form, by Goss (*ibid.*, pp. 698, 1467) to determine electrical dipole moments.

EXPERIMENTAL.

The methods of preparation of pure materials, and of measuring dielectric constants and densities, were essentially the same as those previously described (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668; Jenkins, J., 1934, 480), except that a single solution condenser was used. This condenser is made of metal so far as possible (of brass, plated with platinum) and is designed so that it can easily be taken apart for cleaning but can be accurately re-assembled. The earthed electrode consists of a cylindrical jacket A (see Fig. 1), closed at the bottom, and a lid B, which is located uniquely by a pin in A and is held down by six screws. The lid carries a short piece of quartz C affixed coaxially with it into an annular channel D by means of solder (3 parts ead, 1 part tin). This tube carries and insulates a metal head E, affixed to it by solder, into which fits a stiff rod F which is located uniquely by a steady pin H and is pulled up tightly to the head E by a milled nut I, which in turn is locked by another one J that is also a terminal. The rod passes down through a hole in the lid and supports a cylinder G inside the earthed jacket;

the bottom of the insulated cylinder is a flat cone, so that no air bubbles may be entrapped. In order that as few lines of force as possible may pass through two media when solutions are in the cell, an attempt has been made to make the lines of force near the liquid surface (which is about 1 cm. below the lower side of the lid) run along radii of the cylindrical jacket, by having only a small clearance between the upper edge of the insulated cylinder and the jacket, and by cutting a depression in the top face of the cylinder. The air capacity is about 25 $\mu\mu$F. The condenser is made to take an interchangeable set of electrodes; the plug K can be replaced by a solid cylinder, and the solid cylinder G by a larger hollow one, so that the air capacity is approximately doubled.

FIG. 1.
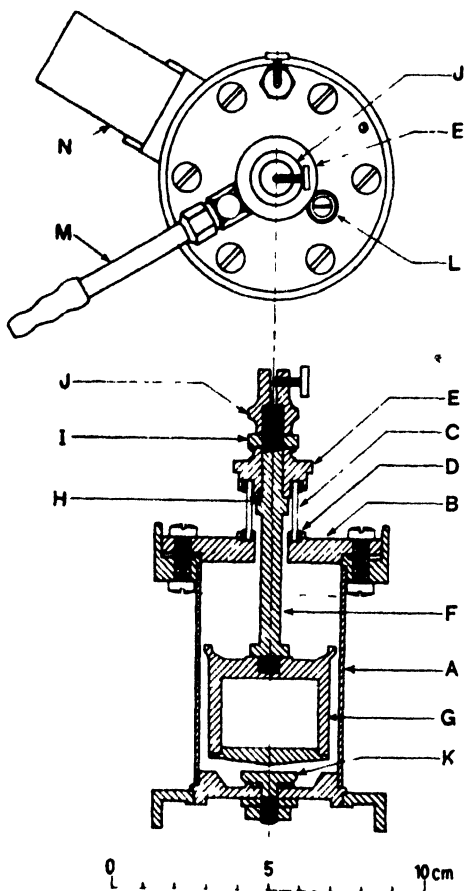
FIG. 2.
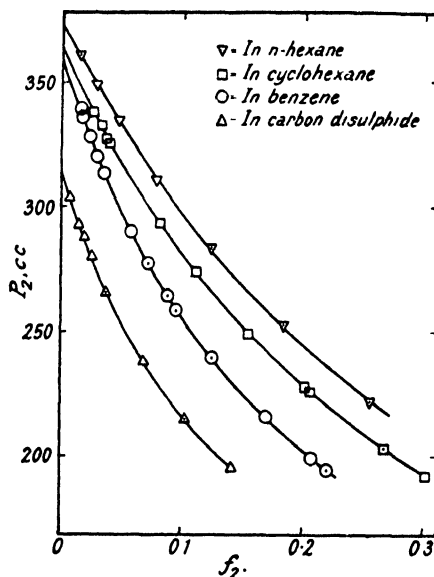
The condenser is filled through a hole in the lid, which can be closed with the screw plug L, with rather more solution than is required, and the excess above a certain level is then withdrawn by a special pipette, so that a definite volume of solution is left in the condenser. In order to prevent the ingress of moisture, a small positive pressure of dry air is maintained inside the condenser through the lead-in tube M; the efficacy of this method was shown on several occasions by the fact that the dielectric constant of carefully dried benzene, which is very hygroscopic, remained constant for several hours. The condenser is held in a thermostat by means of a tongue N which fits into a holder.

That the condenser is satisfactory was shown by the following facts : (*a*) reasonable concordance was obtained with Lange's results (*Z. Physik*, 1925, **33**, 169) in benzene and carbon disulphide solutions, corrected to 25°; (*b*) the polarisations in the more dilute regions of these concentrated solution runs are consistent with the results in dilute solution previously obtained (Jenkins, *loc. cit.*) by using a different condenser; (*c*) the value found for the dielectric constant of

chlorobenzene, a substance easily obtained pure, was 5·611, which is almost identical with that, 5·612, found by Sugden (J., 1933, 768), using a resonance apparatus and a condenser of different air capacity and type; (d) the value found for the dielectric constant of chloroform was 4·737, while that found by Ball (J., 1930, 596) was 4·724.

All the measurements were made at 25·0°. The results are given in the following tables where f_2 is the molecular fraction of nitrobenzene, $\epsilon_{25°}$ the dielectric constant at 25·0°, $d_4^{25°}$ the density, and $_TP_2$ the total polarisation of the solute.

TABLE I.

f_2.	$\epsilon_{25°}$.	$d_4^{25°}$.	$_TP_2$.	f_2.	$\epsilon_{25°}$.	$d_4^{25°}$.	$_TP_2$.
Nitrobenzene in benzene.				*Nitrobenzene in carbon disulphide.*			
0·0000	2·273	0·8736	—	0·0000	2·633	1·2558	—
0·0575	3·597	0·8954	289·9	0·0375	3·888	1·2508	266·0
0·0715	3·928	0·9008	277·4	0·0690	4·986	1·2468	238·0
0·0880	4·326	0·9068	264·2	0·1034	6·218	1·2426	214·9
0·0950	4·490	0·9092	258·8	0·1411	7·579	1·2378	195·3
0·1244	5·224	0·9202	239·8				
0·1695	6·372	0·9365	215·8	*Nitrobenzene in n-hexane.*			
0·2078	7·373	0·9502	199·4	0·0000	1·887	0·6615	—
0·2202	7·704	0·9545	194·8	0·0783	3·043	0·6974	310·6
				0·1236	3·810	0·7181	283·5
Nitrobenzene in cyclohexane.				0·1842	4·940	0·7458	252·5
				0·2559	6·461	0·7800	222·6
0·0000	2·016	0·7739	—				
0·0323	2·573	0·7860	332·7	*Nitrobenzene in carbon tetrachloride.*			
0·0814	3·489	0·8053	293·3	0·0000	2·228	1·5848	—
0·1117	4·100	0·8171	273·8	0·0848	4·066	1·5522	276·4
0·1545	5·014	0·8343	249·7	0·1612	5·814	1·5229	226·9
0·2021	6·131	0·8534	228·0	0·2053	7·114	1·5061	210·9
0·2067	6·236	0·8554	225·8	0·2295	7·771	1·4968	201·4
0·2677	7·777	0·8798	203·0				
0·3018	8·707	0·8942	192·0				

DISCUSSION OF RESULTS.

The P_2–f_2 curves for nitrobenzene in the four solvents *n*-hexane, *cyclo*hexane, benzene, and carbon disulphide, of dielectric constants 1·887, 2·016, 2·273, and 2·633, are given in Fig. 2 : values of $_\infty P_2$ and P_2 in dilute solution have been taken from a previous paper (Jenkins, *loc. cit.*). It is seen that the curves are displaced from one another in the order of the dielectric constant of the solvent, and also that the *cyclo*hexane curve is perfectly normal, which indicates that in this case there is no close relation between degrees of association calculated by the two methods.

Sugden has reported (*Nature*, 1934, **133**, 415; *Trans. Faraday Soc.*, 1934, **30**, 720) an empirical relation between the total polarisation of the solute ($_TP_2$) at any concentration, and the volume polarisability, $(\epsilon - 1)/(\epsilon + 2)$, of the solution. It is

$$_TP_2 = \alpha + {}_T^aP_2 - {}_0^aP_2\{(\epsilon - 1)/(\epsilon + 2)\}$$

where α is a small constant, ${}_T^aP_2$ is the total polarisation deduced from vapour measurements (Sugden uses $_HP_2$), and ${}_0^aP_2$ is the orientation polarisation obtained from the same source.

In order to test the validity of this equation, answers to four questions have to be sought. (a) Is the equation of the right form for a solute in one particular solvent at one temperature? (b) Is the arbitrary constant α independent of solute, solvent, and temperature? (c) Is the slope of the $_TP_2$–$(\epsilon - 1)/(\epsilon + 2)$ line, for one solute at one temperature, independent of the solvent? (d) Is this slope equal to $- {}_0^aP_2$?

(a) Fig. 3 shows such total polarisation–volume polarisation curves for nitrobenzene in different solvents, for concentrations ranging from infinite dilution to pure nitrobenzene : for the sake of clearness, the origin of ordinates has been displaced regularly for each solvent. The dielectric constant of pure nitrobenzene has been taken from Ball (*loc. cit.*) and Sugden (*loc. cit.*), and the density calculated from an equation given by Tyrer (J., 1914, **105**, 2544). It is seen that the benzene curve is almost perfectly straight over the entire range of concentration, but that the other solvents all give a curvature over the range as a whole as indicated by the broken lines. Such curvature has already been found for nitrobenzene

in decane (di*iso*amyl) and *p*-xylene by Fairbrother (*loc. cit.*), and it is therefore quite clear that for this particular solute, in most non-polar solvents, the Sugden equation is approximately, but not exactly, of the right form.

(*b*) In answer to the second question, if the slight curvature noted above be ignored, and mean straight lines be drawn through the concentrated solution points for each solvent, then it is found that the intercepts on the $_TP_2$ axis when $(\epsilon - 1)/(\epsilon + 2) = 0$ (*i.e.*, when $\epsilon = 1$) are different, and therefore, if they are put equal to $\alpha + \frac{o}{T}P_2$, that α varies with the solvent. Alternatively, since the intercepts at $(\epsilon - 1)/(\epsilon + 2) = 1$ (*i.e.*, $\epsilon = \infty$)

FIG. 3.

> O· *In benzene.*
> □· *In cyclohexane.*
> △· *In carbon disulphide.*
> ▽· *In n-hexane.*
> ◊· *In carbon tetrachloride.*
> ●· $_TP_2$ *ordinates for* $_TP_2$ *in carbon tetrachloride.*
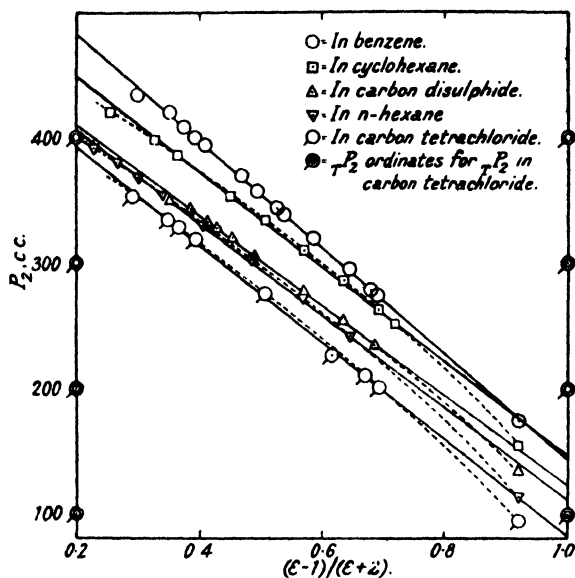
are also found to vary, and since these should be the sum of α and the atom and the electron polarisation, then again α is found to vary. These intercepts are given in Table II, which includes some results obtained by Lange (*loc. cit.*) for solutions in toluene. Furthermore, the value of α determined from the lower intercept for chlorobenzene in benzene solution, using the data of Rolinski (*Physikal. Z.*, 1928, **29**, 660), is not more than 1 c.c., whereas for nitrobenzene it is of the order of 30 c.c., for quinoline in benzene it is 18 c.c., for benzonitrile in benzene it is about 13 c.c., and for ethyl ether in benzene it is 28 c.c. That α depends upon both the solvent and the solute is thus clear.

TABLE II.

Nitrobenzene in different solvents.

Solvent.	Intercept at $(\epsilon - 1)/(\epsilon + 2) = 0.$	Intercept at $(\epsilon - 1)/(\epsilon + 2) = 1.$	Slope.
Benzene	489	64	−425
Carbon tetrachloride	472	82	−390
Carbon disulphide	445	81	−364
n-Hexane	459	94	−365
*cyclo*Hexane	467	86	−381
Toluene	483	64	−419

The third part of the second question, regarding the temperature independence of α, has already been answered by Fairbrother, who found that for nitrobenzene in decane the intercepts at $(\epsilon - 1)/(\epsilon + 2) = 1$ appeared to be equal to within the limits of experimental error, but that if the intercepts at $(\epsilon - 1)/(\epsilon + 2) = 0$ have the significance attributed to them by the equation, then α must decrease with increasing temperature, because the

moment calculated from the variation of the intercepts with temperature is abnormally high (see p. 614).

(c) An answer to the third question can be obtained from Fig. 3, which shows that the slopes differ appreciably for nitrobenzene in different solvents at the same temperature. It appears that the benzenoid solvents, or the non-benzenoid solvents, are fairly consistent among themselves, but differ appreciably from each other in their effects upon the slope. The mean slopes are given in Table II, the variation being $\pm 7\%$ of the average slope.

(d) The results given in Table II are relevant also to the fourth question. Since the gas orientation polarisation for nitrobenzene at $25 \cdot 0^\circ$ is 367 c.c. (calculated from the results of Groves and Sugden, J., 1934, 1094, and McAlpine and Smyth, *J. Chem. Physics*, 1935, **8**, 55), it is obvious that those for nitrobenzene in the non-benzenoid solvents at $25 \cdot 0^\circ$ confirm the conclusion of previous workers, that the slope multiplied by minus one is indeed very close to the gas polarisation : the slopes in the benzenoid solvents, on the other hand, are about 14% too great. In order to test this more generally, further data were collected from the literature, and a representative selection is given in Table III. The selection was made with several requirements in mind. One was that the solutes should be of as many different types as possible, another that in some cases the same solutes should be taken in different solvents, and a third that the gas orientation polarisation should have been determined experimentally in most cases. Some solutes are included, however, which are so polar that there is very little hope of determining the moments from the vapour, so that it is very interesting to see how likely a value is obtained from the Sugden relation. In Table III, col. 1 gives the solute, col. 2 the solvent, and col. 3 the temperature at which the polarisations were measured. Col. 4 gives the slope, multiplied by minus one, of the approximate straight line given by the Sugden relation, and col. 5 the orientation polarisation as calculated from the best values available for the dipole moment, the values determined in the vapour phase being taken when possible (these are marked with a subscript $_G$); col. 6 gives the ratio of the slope of the Sugden relation to the experimentally determined orientation polarisation value, and col. 7 the square root of this ratio, which is the ratio of the moments which would be obtained by using the two ways of calculating the orientation polarisation. The data were obtained from papers which are referred to in " A Table of Dipole Moments " (*Trans. Faraday Soc.*, 1934, **30**, Appendix).

Solute.	Solvent.	Temp.	$-$Slope	$_0P_2$.	$-\dfrac{\text{Slope}}{_0P_2}$.	$\sqrt{-\dfrac{\text{Slope}}{_0P_2}}$.
Et$_2$O	C$_6$H$_6$	18°	9·2	28·0$_G$	0·328	0·5727
	CCl$_4$	25	23·2	27·4$_G$	0·847	0·9203
CH$_3$·CO$_2$Et	C$_6$H$_6$	25	133	64·1$_G$	2·075	1·4404
	CCl$_4$	25	98·4	64·1$_G$	1·535	1·2389
CHCl$_3$	CCl$_4$	25	20·8	20·7$_G$	1·005	1·0025
COMe$_2$	C$_6$H$_6$	22	170	169·8$_G$	1·001	1·0005
	CCl$_4$	25	217	168·1$_G$	1·291	1·1362
C$_5$H$_7$N	C$_6$H$_6$	18	115	100·7	1·142	1·0686
SbCl$_3$	C$_6$H$_6$	25	1115	322	3·463	1·8609
	CS$_2$	25	2240	322	6·956	2·6375
o-NO$_2$·C$_6$H$_4$·CN	C$_6$H$_6$	25	1160	790	1·468	1·2116
m-	C$_6$H$_6$	25	360	296	1·216	1·1027
NO·C$_6$H$_4$·NMe$_2$	C$_6$H$_6$	25	1867	985	1·895	1·3766

From the preceding results it must be concluded that, although some solutes in particular solvents obey the Sugden relation very well, yet other solutes which are quite as normal, or the same solutes in equally normal solvents, fail to do so. Usually the slope is too great, but in one case it is much too small; furthermore, although benzene gives more anomalous results for some solutes than does carbon tetrachloride, the reverse is true in other cases. Hence it seems impossible to formulate any general rules about the discrepancies. Since from the empirical rules of both Müller (*Physikal. Z.*, 1933, **34**, 689) and Jenkins (*Nature*, 1934, **133**, 106) it is unlikely that the true orientation polarisation would be more than 20% greater than the value observed in benzene or carbon tetrachloride, it follows that neither o-nitrobenzonitrile nor p-nitrosodimethylaniline obeys the Sugden relation, the slopes being too great. The most marked anomalies are for antimony trichloride, and since these are so great, they may indicate some unusual solvation effects.

The general conclusions from all these tests may be briefly summarised. For one solute in one solvent, at one temperature, the Sugden relation is approximately, but not exactly, of the right general form. The empirical constant α can vary from 1 to 30 c.c. for different solutes in one solvent, and from 30 to 60 c.c. for one solute in different solvents; moreover, it may vary with temperature (see p. 612). The slope is not, in general, equal to $_0^0P_2$, although in some cases there is close agreement, so that the relation may have a physical significance akin to, but not quite so simple as, the one first given.

The qualitative explanation which Sugden gave for expecting the slope to be the orientation polarisation in the gas was that the diminution of the orientation polarisation by dipole association would be expected to be a function of the volume polarisation, $(\epsilon - 1)/(\epsilon + 2)$, but since this quantity was conceived from a physical model in which association was not considered, it is not clear why it should be a parameter for association.

The equation which Goss derived (*Trans. Faraday Soc.*, 1934, **30**, 751) from the Raman–Krishnan modification (*Proc. Roy. Soc.*, 1928, **A**, **117**, 595) of the Clausius–Mosotti–Debye equation is

$$_TP_2 = {}_T^0P_2 + \{(\epsilon - 1)/(\epsilon + 2)\}(N\psi + N^2\Theta/3RT)$$

where ψ and Θ involve the effect of the anisotropy of the medium on $_EP_2 + {}_AP_2$ and on $_0P_2$ respectively. It has the same form as the Sugden relation, but differs from it in that the slope is $(N\psi + N^2\Theta/3RT)$ instead of $- {}_0^0P_2$, and that it includes no constant α. The difference in meaning attached to the slope in this and in the Sugden relation is unimportant at present, because the meaning which Sugden gave is, according to the present results, not generally correct, and because, ψ and Θ being known for but few substances, the general correctness of the meaning given by Goss cannot be tested. On the other hand, the fact that the experimental data call for a constant α which is not accounted for by the theory shows that the latter is imperfect. Raman and Krishnan elaborated the treatment given by Clausius and Mosotti to the problem of calculating the field on a molecule in a polarisable medium by allowing for the anisotropy of the medium outside the conventional cavity (which they took to be ellipsoidal). They neglected, however, the forces from the molecules inside the cavity, and therefore their relation, like the simple Clausius–Mosotti–Debye relation, should not apply for pure liquids or concentrated solutions of them. In such cases the total polarisation, $_TP_2$, will usually be too small; hence the slope of the total polarisation curve plotted against the volume polarisation will be too steep, and to a first approximation there should be a positive constant α included in the intercept on the polarisation axis where the volume polarisation is zero : this constant would be expected to depend upon solute, solvent, and temperature, all of which factors affect the conditions inside the cavity. As we have seen, this is actually the case, although it should be added that this explanation alone appears insufficient to account for the considerable values of α relative to $_TP_2$ found in some cases. Since it would be expected that the deviation of the actual curve from the ideal curve would not be linear but would increase with the concentration of the polar substance, it is not surprising to find that the curves, to a second approximation, are not straight but are concave relative to the abscissæ.

For these reasons, the simple method proposed by Goss (*loc. cit.*) to calculate a correct dipole moment cannot be of general validity; for even though the difference of the intercepts on the total polarisation axis, at $(\epsilon - 1)/(\epsilon + 2) = 0$, of two curves at two temperatures be used, the variation of α with temperature would vitiate the result, as pointed out by Fairbrother (*loc. cit.*). From the suggested origin of α it would be expected that it would decrease as the temperature increases, so that the apparent change of orientation polarisation found would be too large, and the values of the moments would be too high. In actual fact, Goss obtains moments of 1·20 D and 1·78 D for chloroform and methylene chloride respectively, whereas the values determined from the vapours are 1·00 D and 1·61 D (Sänger, *Physikal. Z.*, 1926, **27**, 556; Mahanti and Sen Gupta, *J. Indian Chem. Soc.*, 1928, **5**, 673; Sircar, *Indian J. Physics*, 1928, **3**, 673). Fairbrother's data (*loc. cit.*) for nitrobenzene lead to a value of about 4·5 D, whereas the values from vapour measurements are 4·19 D (McAlpine and Smyth, *loc. cit.*) and 4·23 D (Groves and Sugden, *loc. cit.*).

Since, as has been seen, there is no clear theoretical justification for expecting that the

slope of the total polarisation–volume polarisation line would be $- \frac{9}{5}P_2$, and since in fact it frequently is not, the method of determining electric dipole moment proposed by Fairbrother also cannot be of general use. That the method gives a good mean value for nitrobenzene is fortuitous, as is emphasised by the drift of apparent moment with temperature, from $4 \cdot 30 D$ at $20°$ to $4 \cdot 19 D$ at $120°$.

SUMMARY.

Electric polarisations of concentrated nitrobenzene solutions in benzene, carbon disulphide, *n*-hexane, *cyclo*hexane, and carbon tetrachloride have been determined. The nitrobenzene–*cyclo*hexane curve has been shown to be of normal type.

The Sugden relation has been discussed in the light of these results, and its use by Fairbrother and by Goss to evaluate electric dipole moments has been shown to have no general justification. A suggestion is made that the Goss method is in error on account of the approximate nature of the argument used by Raman and Krishnan in deriving their formula.

136. *An X-Ray Study of the Structure of the Phthalocyanines. Part I. The Metal-free, Nickel, Copper, and Platinum Compounds.*

By J. MONTEATH ROBERTSON.

THE phthalocyanines, recently described by Linstead and his collaborators (J., 1934, 1016), form a series of beautifully crystalline compounds which are remarkable for their great stability, the copper derivative subliming unchanged at $580°$. Phthalocyanine itself, containing only carbon, hydrogen, and nitrogen, is hardly less stable. Further interest attaches to these compounds, as Linstead has pointed out, on account of their value as pigments, their structural relationship with the natural porphyrins, and finally, in connexion with the stereochemistry of the metals with which they combine. X-Ray analysis is undoubtedly the most powerful method for dealing quantitatively with the last aspect.

Owing to the great size and complexity of the molecules, it has not yet been possible to locate all the individual atoms in the crystal unit. Such a task would require the precise measurement of many hundreds of reflexions and involve the determination of 60 parameters for the carbon and nitrogen atoms alone. By a fortunate circumstance, however, the crystal structures of the parent phthalocyanine and many of the metallic derivatives are dimensionally so similar that direct comparisons can be made between the intensities of corresponding reflecting planes in the different compounds. By this means the main outlines of these structures are already clear. It is best, therefore, to commence by making a comparative study of the various compounds. The way is then cleared for complete structure determinations by quantitative intensity measurements.

Crystal Data.—The writer is greatly indebted to Dr. Linstead and Dr. Dent for supplying well-formed crystals of phthalocyanine and its copper, nickel, and platinum derivatives. By low-pressure sublimation in a current of carbon dioxide at temperatures above $500°$, these were obtained as long needles or laths. The crystals are all monoclinic, the needle axis corresponding with the *b* axis in the following description. The cross section was usually small, especially in the platinum compound, but in the other three compounds fine laths were obtained, measuring $0 \cdot 1$ by $0 \cdot 3$ or $0 \cdot 4$ mm., and sometimes 1 cm. or more in length, which were very suitable for the X-ray work. No definite end faces were observed, the growth of the crystal being generally terminated by fracture across the lath. In the metal-free compound the $(20\bar{1})$ and the (001) face were developed, the latter being especially prominent. Apart from the somewhat phenomenal elongation along the *b* axis, the habit is very similar to that of many organic crystals, with some tendency to cleavage in the

(001) and (20$\bar{1}$) planes. The most perfect natural faces were observed in copper phthalo-cyanine, where the (001), (100), (20$\bar{1}$), and (10$\bar{1}$) planes were found, as in Fig. 1. Some specimens of this compound were twinned on (001).

The X-ray work was carried out by means of rotation, oscillation, and moving-film photographs, with copper radiation. The absorption of rays of this wave-length ($\lambda = 1.54$) by the metal compounds is somewhat high, but by employing small specimens (0.005—0.01 mg.) excellent results were obtained. The cell dimensions and other constants are collected in Table I. The linear measurements should be accurate to about 0.5%. The observed halvings of {$h0l$} when h is odd and of {010} were obtained from long-exposure moving-film photographs (compare Plate I). Between 100 and 200 {$h0l$} reflexions were observed from each crystal, without yielding any exception to the general halving. To establish the {010} halving, only a few reflexions are available ($d_{010} = 3.81$—4.79 Å.). Prolonged exposures were taken about the a and c axes, and this halving was established for phthalocyanine and the copper and the nickel compound up to the (050), and for the platinum compound up to the (030). The (020) and (040) reflexions are definite, but weak.

FIG. 1.

Copper phthalocyanine.

FIG. 2.

End view of phthalocyanine molecules.
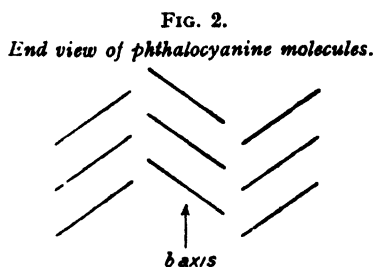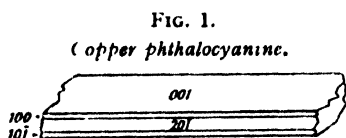
These results definitely establish that the space group is $P2_1/a$ and, consequently, that the molecule has a centre of symmetry. It may be noted that with the above halvings it is not possible to relegate the crystal to a lower symmetry class which does not require the centre of symmetry. Owing to the important deductions concerning the structure which follow from the centro-symmetry, it seemed worth while to make additional tests of the presence or absence of pyro-electric or piezo-electric effects in the crystal. Some well-formed crystals of copper phthalocyanine were selected for the test, measuring about 0.5 by 0.1 mm., and 12 mm. long. Two such crystals were attached to fine silk fibres and immersed in liquid air. No attraction between the crystals was observed while the temperature was thus falling rapidly, or upon removal while the temperature was rising. As a control, two small crystals of resorcinol gave a very large effect, while two small crystals of s.-triphenylbenzene, which is weakly polar, gave a smaller but quite definite effect. The negative result for copper phthalocyanine is in conformity with the X-ray evidence.

TABLE I.

	Phthalo-cyanine.	Nickel deriv.	Copper deriv.	Platinum deriv.
a, Å.	19.85	19.9	19.6	23.9
b, Å.	4.72	4.71	4.79	3.81
c, Å.	14.8	14.9	14.6	16.9
β	122.25°	121.9°	120.6°	129.6°
Space group	$C_{2h}^5 (P2_1/a)$	$C_{2h}^5 (P2_1/a)$	$C_{2h}^5 (P2_1/a)$	$C_{2h}^5 (P2_1/a)$
Mols. per cell	2	2	2	2
Molecular symmetry	Centre	Centre	Centre	Centre
Vol. of unit cell	1173 Å.³	1186 Å.³	1180 Å.³	1186 Å.³
d (found)	1.44	1.63	1.63	1.98
d (calc.)	1.445	1.59	1.61	1.97
M	514	571	576	707
No. of electrons per unit cell, F (000)...	532	584	586	684

General Structural Considerations.—The dimensional similarity of the first three crystals indicates at once that the molecule must consist of a large rigid framework which suffers no appreciable distortion by the entrance of the metal atom. One must assume that in the

PLATE 1

{20Ī}   {200}   {001}   {20Ž}   {201}
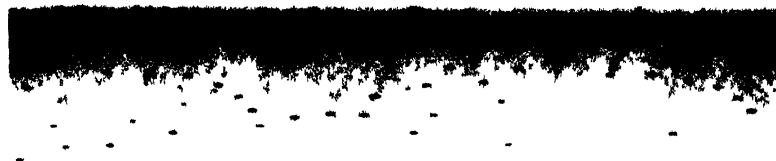
Phthalocyanine {h0l}
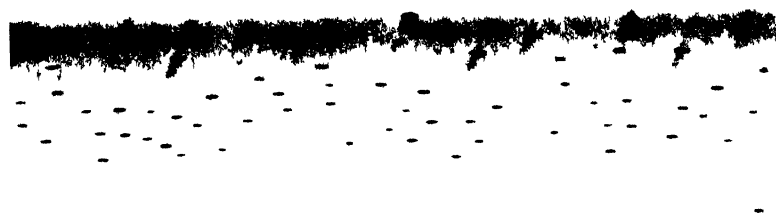
Nickel phthalocyanine {h0l}
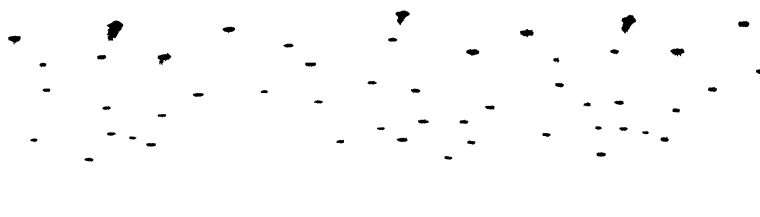
Copper phthalocyanine {h0l}
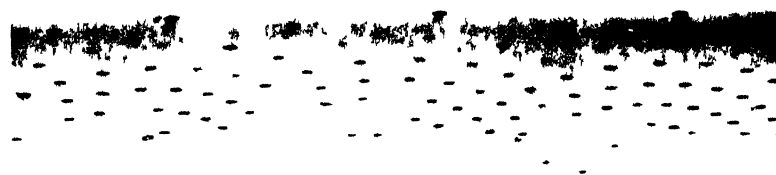
Platinum phthalocyanine {h0l}

metal-free phthalocyanine there exists some cavity, perhaps sparsely occupied by two imino-hydrogen atoms, which can accommodate the various metallic elements. The small alteration in the dimensions of the copper compound, and the more abrupt change in the platinum compound, are more probably accounted for by a change in the *orientation* than by any change in the molecular dimensions. In the platinum compound, for example, the *b* axis decreases in length by 1 Å., but the area of the *ac* face increases in proportion, so the volume of the cell remains constant.

The figures show that one molecule is contained in a space of $\frac{1}{4}abc$ sin β or about 9·9 × 12·5 × 4·7 Å.³ for the first three compounds, and of about 12·0 × 13·0 × 3·8 Å.³ for the last. This at once points to large, square, and probably flat molecules, well spread out in the *ac* plane. The platinum phthalocyanine molecules are obviously flattened out still more in this plane. Molecules of identical orientation recur at intervals of 4·7 or 3·8 Å. along the *b* axis. Now the minimum distance of approach between aromatic hydrocarbon rings in the solid state is known to be about 3·6—3·7 Å. (Report of International Conference on Physics, 1934, Part II, p. 46), a value which may be taken as a measure of the " thickness " of such molecules. Hence, although the molecules of the first three compounds may be inclined to the *ac* plane at angles up to 35° or 40°, and platinum phthalocyanine at 10—20°, yet there is no possibility of any of these molecules being interleaved by the adjacent (reflected) molecules. When viewed end-on, the molecules are probably arranged in a manner such as is shown in Fig. 2, the lines indicating their mean planes. Thus a projection of the structure along the *b* axis, on the (010) plane, will give a complete picture of the molecule and all its component atoms. The possibility of such a simple projection is rarely encountered in organic crystal structures, for, even in such comparatively simple examples as naphthalene and anthracene, many of the individual atoms are obscured by overlap, either from within the molecule, if it is viewed from a high angle, or from interleaving molecules, if they are more nearly normal to the projection axis.

From the cell dimensions, space group, measured density, and metal content of these compounds, it is possible to calculate the molecular weights to within about 5% (*Nature*, 1935, **135**, 506). The results agree with those required by Linstead's formulæ, (I)—(IV), but it is impossible to determine the number of hydrogen atoms in the molecule by this method. It is, however, clearly established that the unit cell contains two centro-symmetric molecules. An important deduction immediately follows regarding the symmetry of the central group. *The metal atom and the four surrounding* iso*indole nitrogen atoms must all lie strictly in one plane.* For the metal atom, being unique, must coincide with the centre of symmetry. If a straight line be drawn from the centre of one of the nitrogen atoms to the centre of the metal atom and produced an equal distance beyond, it will touch the centre of the opposite nitrogen atom, by the definition of a centre of symmetry. The metal atom and the other two nitrogen atoms must similarly lie on another straight line. Hence it is possible to describe a plane containing these two straight lines and the five atom centres situated on them.

There is as yet no direct experimental evidence from the X-ray work that the whole molecule is planar. We may, of course, choose any two pairs of centro-symmetric points, *e.g.*, on the extracyclic nitrogen atoms, or at the centres of the benzene rings, and show that they lie on a plane containing the central metal atom; but these various planes need not coincide.

Linstead has shown (J., 1934, 1037) that the chemical evidence is in favour of formula (I) for phthalocyanine and (III) for the metal derivatives, the metal displacing the two imino-hydrogen atoms and being bound by covalencies to the two *iso*indole nitrogen atoms, and probably co-ordinated to the other two. He also points out that from general stereo-chemical considerations " the cyclic framework of phthalocyanine (I) should exist in one plane, and the only possibility of deviation lies in the ability of ring A to rotate about the two single links connecting it to the extracyclic nitrogen atoms." We have just seen, however, from the crystal evidence, that any two pairs of centro-symmetrical points and the centre itself are necessarily coplanar. Hence, in the crystal, ring A cannot deviate from the great plane of the molecule. It would seem to follow from the stereochemistry (Linstead, *loc. cit.*) that the two imino-hydrogen atoms in (I) must lie out of the great plane,

giving rise to the possibility of a *cis-* and a *trans-*form.   Only the latter is strictly compatible with the centre of symmetry.
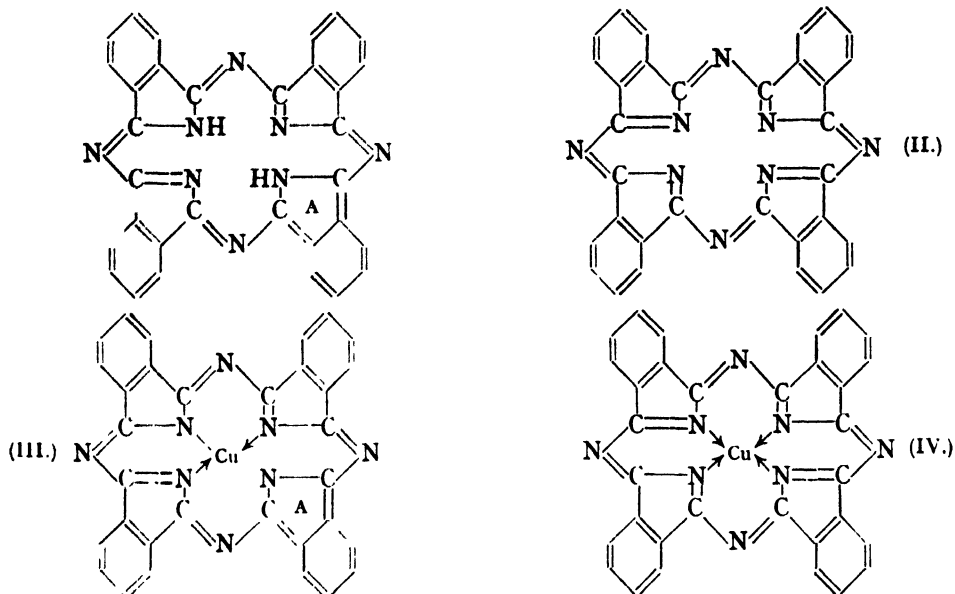
A few difficulties remain with regard to the fine structure.   Formulæ (II) and (IV), which contain no imino-hydrogen and represent the metal atom as bound by four co-ordinate links, are perfectly centro-symmetrical and thus completely satisfy the crystal evidence ; but Linstead shows that the chemical evidence and the physical properties of the copper compound are rather definitely in favour of (I) and (III), which necessitate one *o*-quinonoid and three benzenoid rings.   The difficulty of reconciling these formulæ with the centro-symmetry displayed in the crystal is not, however, very great.   The problem is analogous to that encountered in reconciling the ordinary Kekulé formula for benzene to the centro-symmetry displayed by symmetrically substituted benzene derivatives in the crystalline state   In the phthalocyanine structure we must regard the whole molecule as one continuously conjugated system, so that the *o*-quinonoid ring does not possess a definite location in the structure.   This is not in conflict with the chemical evidence.

Were the *o*-quinonoid ring fixed in the molecule, the distortion of interatomic distances produced would be sufficient to destroy the exact centre of symmetry,* unless this centre were not a true one, but a statistical centre derived from a random distribution of molecules in the crystal.   The structure and general condition of the crystal seem too perfect for this latter supposition to be a likely one.

Evidence from Intensities.—The intensities of the X-ray reflexions are in general agreement with the structures deduced by Linstead.   This evidence is of a much more searching and detailed character than the general considerations of dimensions and symmetry with which we have so far dealt ; if successfully completed, it should furnish accurate information regarding the exact situation of every atom in the molecule ; but owing to the great complexity of the molecules only a qualitative survey and comparison of the different compounds is attempted below.

The {*h*0*l*} zone, which corresponds to a projection of the structure on the (010) plane, contains by far the greatest range of reflecting planes.   This zone was studied by means of moving-film photographs of crystals rotated about the *b* axis.   Typical exposures for the four compounds are shown in Plate I, all taken with copper radiation.   When we pass from phthalocyanine to the nickel derivative, the *intensity* of many of the reflexions is seen to change abruptly ; many planes which were absent or too weak to be visible now appear

* See analysis of benzoquinone (*Proc. Roy. Soc.*, 1935, *A*, in the press).

owing to the extra contribution which the central nickel atom (atomic number 28) makes to the scattering. The *position* of corresponding reflecting planes, however, is almost identical, because the lattice dimensions are so similar. The photograph obtained from the copper derivative is practically identical with that of the nickel derivative, as regards both dimensions and intensities.* This is to be expected, because copper (atomic number 29) has practically the same scattering power for X-rays as nickel. In the photograph obtained from the platinum compound, however, there is a striking alteration. Almost every possible reflecting plane is represented, and the intensity distribution is very uniform. Platinum (atomic number 78) is equal to 13 carbon atoms in scattering power for X-rays, and the effect of this concentration of scattering matter at the centre of the molecule is to swamp all the reflexions, and produce a nearly uniform distribution of intensity. To a rough first approximation, this structure may be considered as an open lattice of platinum atoms 12—13 Å. apart. Occasionally, a number of the other atoms combine to reinforce or diminish the reflexions, a possibility which becomes of more frequent occurrence as the higher orders are reached.

Table II gives some observations on the intensities of certain reflexions which help to settle the orientations of the molecules in the crystals. Fig. 3 shows the positions of the

FIG. 3.
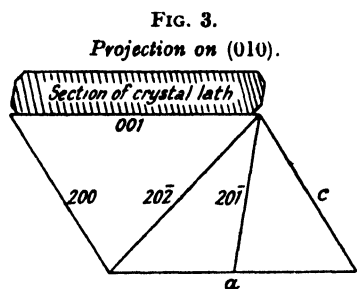
Projection on (010).

FIG. 4.

Symmetrical model of phthalocyanine molecule.

○ *Carbon.*
● *Nitrogen*
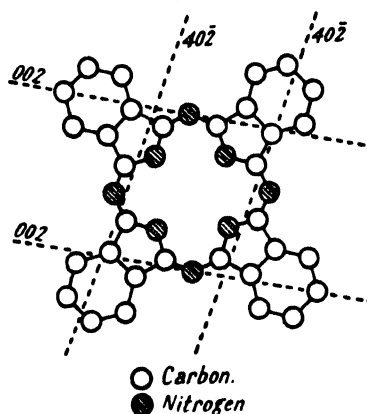
trace of some of these planes on the (010) projection of nickel, copper, and metal-free phthalocyanine. It will be observed that the (001) and (20$\bar{1}$) are nearly perpendicular to each other (80°); so also are the (200) and (20$\bar{2}$) (76°). Now, from Table II, it will be seen that the intensity distribution in the successive orders of the (001) and the (20$\bar{1}$) series shows a very marked correspondence. The same is true of the successive orders of the (200) and the (20$\bar{2}$) series. This applies to all four compounds, and is most pronounced in the platinum derivative. The intensity of the successive orders of any given plane depends upon the average distribution of atoms normal to the plane. Hence the above results show that this average distribution is very similar in directions (arbitrarily chosen) which are nearly 90° apart. In other words, the molecule at least approximates to four-fold symmetry in its detailed structure.

If we make a symmetrical model based on the chemical structure, it is possible to explain a number of the observed intensities qualitatively. The (002) and the (40$\bar{2}$) planes, seen edge-on, probably occupy roughly the positions shown in Fig. 4 with respect to this model, which may, however, be foreshortened by 10—20% in some direction depending upon the precise inclination of the molecular planes to the (010). Now it can be seen that there is a considerable concentration of atoms near to these planes, and we should

* The size of the crystal specimens and the exposure times necessarily vary a little from one compound to another.

TABLE II.

hkl.	sin θ. λ = 1·54. Phthalo-cyanine.	Phthalo-cyanine.	Ni deriv.	Cu deriv.	Pt deriv.	hkl.	sin θ. λ = 1·54. Phthalo-cyanine.	Phthalo-cyanine.	Ni deriv.	Cu deriv.	Pt deriv.
001	0·062	v.s.	v.s.	v.s.	v.s.	200	0·092	abs.	s.	s.	v.s.
002	0·123	v.s.	m.	m.	m.	400	0·183	s.	abs.	abs.	m.s.
003	0·184	m.	v.w.	v.w.	m.s.	600	0·275	m.s.	s.	s.	s.
004	0·246	v.w.	s.	s.	s.	800	0·367	abs.	m.	m.	s.
005	0·307	m.s.	v.v.w.	v.v.w.	m.	1000	0·458	v.w.	m.	m.	m.s.
006	0·369	m.s.	v.w.	v.w.	w.m.	1200	0·550	v.w.	w.m.	w.m.	m.
007	0·430	w.	m.s.	m.s.	m.s.	$20\bar{2}$	0·107	w.	s.	s.	v.s.
$20\bar{1}$	0·079	v.s.	v.s.	v.s.	v.s.	$40\bar{4}$	0·214	s.	abs.	abs	m.s.
$40\bar{2}$	0·157	v.s.	m.	m.	w.m.	$60\bar{6}$	0·322	m.	m.s.	m.s.	s.
$60\bar{3}$	0·236	m.	v.w.	v.w.	m.s.	$80\bar{8}$	0·427	m.s.	m.s.	m.s.	s.
$80\bar{4}$	0·314	abs.	m.	m.	s.	$100\bar{10}$	0·536	v.v.w.	w.m.	w.m.	m.s.
$100\bar{5}$	0·393	v.w.	w.	w.	m.	$120\bar{12}$	0·643	abs.	w.	w.	m.
$120\bar{6}$	0·471	m.s.	w.	v.v.w.	w.m.	020	0·326	w.	m.	m.	m.s.
$140\bar{7}$	0·549	v.v.w.	w.m.	w.m.	m.s.	040	0·652	v.w.	w.m.	w.m.	—

v.s. = very strong.　　　　　　　　　w. = weak.
s. = strong.　　　　　　　　　　　　 v.w. = very weak.
m.s. = medium strong.　　　　　　　 v.v.w. = just visible.
m. - medium.　　　　　　　　　　　　abs. = absent.
w.m. = weak medium.　　　　　　　　 — = beyond experimental limits.

therefore expect strong reflexions.   These are actually observed in the metal-free compound, but in the copper and the nickel compound these strong reflexions become weak and are replaced by strong second-order reflexions, (004) and (80$\bar{4}$).   This is just what would be expected if the metal atom goes in at the centre of the molecule, because the copper or nickel atom is nearly as effective as 5 carbon atoms in scattering power for X-rays, and so the (002) and (40$\bar{2}$) planes become interleaved with scattering matter.   This orientation of the molecule with respect to the crystal planes is further supported by the way in which adjacent molecules are found to fit together when the structure is extended, a gap of 3—4 Å. existing between atoms on neighbouring molecules.   The orientation given is comparatively rough at present, however, so that a rotation of the molecule by 10°, which would be equivalent to interchanging the indices of the (40$\bar{2}$) and (002) planes in Fig. 4, might be possible.

These observations on the intensities can be extended in a more general form.   The phase constant of the contribution to the structure factor made by the metal atom must always be positive, because the metal atom is situated at the centre of symmetry.   Now if the phase constant of a given reflexion from metal-free phthalocyanine is also positive, *i.e.*, if it corresponds to an average sinusoidal distribution of scattering matter with a maximum at the centre of symmetry, then the corresponding reflexion in the metal compounds will be of greater intensity; but if the reflexion from metal-free phthalocyanine is negative, corresponding to a minimum at the centre of symmetry, then the corresponding reflexion from the metal compounds will show a decrease in intensity, provided that the structure factor of the metal-free reflexion is in this case of greater magnitude than one-half the contribution made by the metal atom alone.   Representing the structure factors of phthalocyanine, the metal atom alone, and of metal phthalocyanine by S_P, S_M, and S_{MP} respectively, we have $S_P + S_M = S_{MP}$.   As S_M is always positive, we can usually determine the sign of S_P by observing the relative magnitudes of S_P and S_{MP}.   To what extent this method can be applied in quantitative work will depend on how closely similar are the orientations of the phthalocyanine and metal phthalocyanine molecules in the crystals.

SUMMARY.

Phthalocyanine and its nickel, copper, and platinum derivatives form a series of closely similar monoclinic crystals, space-group $P2_1/a$, with two centro-symmetrical molecules per unit cell.   The dimensions indicate large, square, and probably flat molecules.   It is shown that the central metal atom and the four surrounding *iso*indole nitrogen atoms are necessarily coplanar.   The bearing of these facts upon the chemical structure is discussed.   In particular, the X-ray evidence, in conjunction with the stereochemical considerations

mentioned by Linstead, shows that the whole molecule, with the possible exception of the two central imino-hydrogen atoms, should exist in one plane.

A general consideration of the intensities of the reflexions shows that the molecules possess at least approximately four-fold symmetry, with concentrations of atoms about where they would be expected from Linstead's structure. The approximate orientations of the molecules in the crystals have been determined. By comparing corresponding reflexions from the metal-free and from the metal compounds, a direct determination of the phase constants of some of the reflexions can be made.

In conclusion, I wish to thank Dr. Linstead and his collaborators for the many finely crystalline samples of these compounds which they have prepared for this work. To Sir William Bragg and the Managers of the Royal Institution I am indebted for the facilities afforded at the Davy Faraday Laboratory.

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137. *The Planar Configuration of Diamagnetic Nickel Complexes. Part II.*

By H. J. Cavell and S. Sugden.

In continuation of the work described in Part I (J., 1932, 246) the nickel derivatives of methyl-*n*-propyl- and -*n*-butyl-glyoximes have been found to be diamagnetic and to occur in isomeric forms which are readily interconvertible. The m. p.'s of these substances and of the isomeric nickel benzylmethylglyoximes are collected below :

Isomeric Nickel Glyoximes.

Glyoxime.	M. p., α-form.	M. p., β-form.	M. p., equilibrium mixture.
Methyl-*n*-propyl	165°	133°	124°
Methyl-*n*-butyl	150	86	80
Benzylmethyl	168	76	150

To these may be added the two forms of the nickel derivative of methylglyoxal described by Tschugaev (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1466). This substance was obtained in a dark red unstable form and in an orange stable form, but the former is too unstable to give an m. p.

Details of the separation of the propyl and the butyl compounds are given in the experimental part of this paper. The chief difference between these isomerides and the benzyl compounds is the high proportion of the β-form found in the equilibrium mixture produced by fusion. The propyl derivatives crystallise well from acetone on a microscope slide, and the two forms have markedly different crystal habits : the α-form gives loose bundles of long blunt-ended prisms, the β-form rosettes of deeper coloured fine needles.

The occurrence of pairs of isomerides, therefore, seems general for the unsymmetrical nickel glyoximes. As a further test of Pauling's theory (*J. Amer. Chem. Soc.*, 1931, **53**, 1367) that 4-covalent nickel complexes which are diamagnetic may have a planar configuration, we have sought for other compounds of this type. The magnetic data will be published in another paper; the only compounds found which are diamagnetic and sufficiently soluble in organic solvents to enable a search for isomerides to be made are the *NN*-dialkyldithiocarbamates. The n-*propyl* and the n-*butyl* compound have been prepared, and isomerides sought by fusing these substances and fractionally crystallising the products. Each of the dithiocarbamates gave only one form.

The constitution of these complexes may be written with the nickel atom co-ordinated to two sulphur atoms, as in the electronic formula (I), or to sulphur and nitrogen, as in (II).
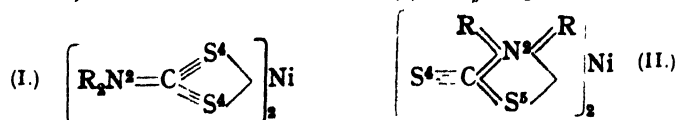
The symmetrical formula (I) seems more probable, and would not give isomeric forms even if the links to the nickel atom had a planar configuration. The failure to find isomerides

may perhaps be taken as negative evidence in favour of (I) rather than (II). Molecular-weight measurements in benzene show that these substances have the formula [Ni, 2X], where X is the dithiocarbamic acid residue.

As a further test of the theory of planar configuration of the nickel glyoximes, we have determined their dipole moments, with the results shown in Table I. Their most probable structure is represented by (III), or by (IV) if the view of Brady and Muers (*J.*, 1930, 1601) is adopted, *viz.*, that the hydrogen atoms of the NOH groups are also co-ordinated. These formulæ show the *trans*-isomerides; the structure for the *cis*-form is obtained by inter-changing the groups R_1 and R_2 in one half of the molecule. Since the central portion of

$$
\begin{array}{cc}
R_1\!=\!C\!=\!C\!=\!R_2 & R_1\!=\!C\!=\!C\!=\!R_2 \\
O^6\!=\!N^1 \quad N^1\!=\!O^4\!=\!H & O^5\!=\!N^1 \quad N^1\!=\!O^5 \\
\text{(III.)} \qquad \searrow\!\!\nearrow & \quad H \quad Ni \quad H \qquad \text{(IV.)} \\
Ni & \\
\nearrow\!\!\searrow & O^5\!=\!N^1 \quad N^1\!=\!O^5 \\
H\!=\!O^4\!=\!N^1 \quad N^1\!=\!O^6 & \\
R_2\!=\!C\!=\!C\!=\!R_1 & R_2\!=\!C\!=\!C\!=\!R_1
\end{array}
$$
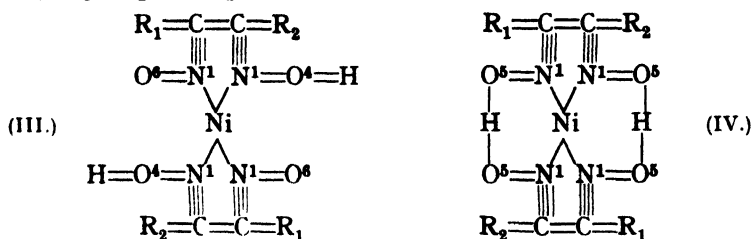
the molecule is symmetrical, the moments should be small if the bonds to nickel are in one plane and the groups R_1 and R_2 are alkyl or aryl radicals. Furthermore, the *cis*- and *trans*-forms should have nearly the same moments.

Owing to experimental difficulties, the moments recorded in Table I can be regarded only as approximate values. They are rather larger than would be expected from (IV), but not larger than might be expected from the rotation of the hydroxyl groups in (III). It will be seen that the α- and β-forms have nearly the same moment.

If the group R_1 has a considerable dipole moment in a definite geometrical position with respect to the nickel atom, then it is clear that the moments of the two R_1 groups would

TABLE I.

Dipole Moments of Nickel Glyoximes.

Glyoxime.	Dipole moment, in Debye units.		Glyoxime.	Dipole moment, in Debye units.	
	α-Form.	β-Form.		α-Form.	β-Form.
Methyl-*n*-propyl	1·4	1·5	Benzylmethyl	1·3	1·6
Methyl-*n*-butyl	1·3	1·3	*p*-Chlorophenyl-*n*-butyl ...	1·8	—

be opposed in the *trans*-form and would reinforce one another in the *cis*-form. Dipole-moment determinations would then give a definite test of the planar hypothesis.

The most suitable group to use in synthesising glyoximes appeared to be *p*-chlorophenyl. *p*-Chlorophenylmethylglyoxime was therefore prepared, but its *nickel* derivative proved to be almost insoluble in benzene. *p*-Chlorophenyl-*n*-butylglyoxime gave a more soluble *nickel* derivative, but difficulties in the synthesis of this oxime have so far prevented the isolation of the lower-melting form, although indications of its existence have been obtained. The higher-melting form gave a dipole moment which is nearly the same as that of nickel glyoximes not containing a polar substituent in the group R_1. This result gives strong support to the view that the nickel glyoximes have a planar configuration, and that the higher-melting forms have the *trans*-configuration. It is difficult to account for the disappearance of the dipole moment of the two C–Cl linkages on any other hypothesis.

EXPERIMENTAL.

*Methyl-*n-*propylglyoxime.*—*n*-Propylacetoacetic ester (1 mol.) was dissolved in 10% sodium hydroxide solution, and sodium nitrite (1 mol.) added. Excess of hydrochloric acid was run slowly into the chilled solution with vigorous stirring, and the oximino-ketone separated as an oil. This was converted without further purification into the glyoxime, which was crystallised from aqueous alcohol; m.p. 175° (Tschugaev, *Z. anorg. Chem.*, 1905, **46**, 147, gives 168°). The nickel derivative was prepared by adding an alcoholic solution of the glyoxime to a cold aqueous solution of excess of nickel chloride and sodium acetate. The red precipitate was well washed

and air-dried; it was moderately soluble in benzene and acetone and less soluble in alcohol and ligroin.

Separation of isomerides. 15 G. of the nickel derivatives were dissolved in the least quantity of cold acetone, and water added slowly. The first precipitate was mostly the α-form, m. p. 160°; after recrystallisation from acetone, it had m. p. 165°, unchanged by further crystallisation. (These and other m. p.'s recorded for nickel glyoximes were determined by plunging the m.-p. tube in a preheated bath and observing whether fusion occurred in 30 secs. The ready interconversion of the isomerides makes m. p.'s meaningless if the specimen is heated slowly.) Tschugaev (*loc. cit.*) gives 144°, and Ponzio (*Gazzetta*, 1921, **51**, 213) 160°, for the m. p.

The separation of the β-form gave difficulty until it was noted that fusion gave a product of m. p. 124°, which contained a large amount of the lower-melting form. The pure β-isomeride, m. p. 133°, was obtained as the first precipitate when this equilibrium mixture was dissolved in acetone and fractionally precipitated with water; the m. p. was unchanged by repetition of this process. Microscopic examination of crystals deposited by evaporation from acetone showed that the product of m. p. 133° was homogeneous, but that of m. p. 122° gave a mixture of crystals exhibiting the habits of the typical α- and β-forms. The α-form could also be obtained from the equilibrium mixture by fractional precipitation of the benzene solution with ligroin.

Both forms gave the same equilibrium mixture on fusion, and regenerated the parent glyoxime when shaken with cold hydrochloric acid (m. p. of glyoxime from α-form 174°, from β-form 175°) (Found, for α-form: Ni, 16·8; for β-form: Ni, 16·5. Calc. for $C_{12}H_{22}O_4N_4Ni$: Ni, 17·0%).

Methyl-n-butylglyoxime.—The intermediate oximino-ketone was prepared from *n*-butylaceto-acetic ester in the same manner as the propyl compound; after crystallisation from ether, it melted at 60°. Oximation gave the glyoxime, which crystallised from aqueous alcohol and melted at 173°. The *nickel* complex was precipitated in cold solutions and melted between 143° and 145°. It was very soluble in benzene and acetone, and part of it readily soluble in ligroin. By recrystallisation from this solvent, the α-form, m. p. 150°, was isolated.

Separation of the isomerides. This was attempted by fractional precipitation with water of solutions of the crude product in acetone, but only mixtures were obtained, varying in m. p. from 100° to 143°. It was then found that fusion of any of these mixtures or of the pure α-form gave an equilibrium mixture of m. p. 80° which was rich in the β-form. This mixture readily gave the β-form of m. p. 86° in the earlier fractions resulting from precipitation by water from acetone solution. The α-form was also isolated from the equilibrium mixture by several recrystallisations from ligroin. Both isomerides gave the same equilibrium mixture on fusion and regenerated the parent glyoxime when shaken with cold hydrochloric acid (Found, for α-form : Ni, 15·6; for β-form : Ni, 15·7. $C_{14}H_{26}O_4N_4Ni$ requires Ni, 15·7%). Molecular weights (cryoscopic) in benzene, at concentrations ranging from 14 to 20 g. per 1000 g. of solvent : α-form, $M = 477, 494$; β-form, $M = 466, 478$ (Calc. : $M = 373$). Both forms show marked association in benzene solution but have the same molecular weight. Similar association was found with the isomeric nickel benzylmethylglyoximes (Sugden, *loc. cit.*).

p-*Chlorophenylmethylglyoxime.*—*p*-Chloropropiophenone, m. p. 35°, was prepared by the Friedel–Crafts reaction from propionyl chloride and chlorobenzene. From this, the *iso*nitroso-ketone was made by the method of Hartung and Munch (*J. Amer. Chem. Soc.*, 1929, **51**, 2262) and melted at 119° after crystallisation from alcohol. Oximation gave the glyoxime, which crystallised from alcohol and had m. p. 223°. The *nickel* derivative, prepared in the usual manner, had m. p. 283° (Found : Ni, 11·5. $C_{18}H_{16}O_4N_4Cl_2Ni$ requires Ni, 12·2%). It was very sparingly soluble in hot benzene, chlorobenzene, and chloroform, and insoluble in ligroin. Its low solubility made it unsuitable for the separation of isomerides or the measurement of dipole moments, so further work on this substance was abandoned.

p-*Chlorophenyl-n-butylglyoxime.*—*p*-Chlorophenyl *n*-amyl ketone was prepared by the Friedel–Crafts reaction from chlorobenzene and hexoyl chloride. The yield was improved, and the separation of the product facilitated, by using 1 mol. of hexoyl chloride, 1·1 mols. of aluminium chloride (Al_2Cl_6), and 3 mols. of chlorobenzene. When the reaction was complete, the product was poured into cold water to decompose the excess of aluminium chloride. This gave an emulsion owing to the separation of solid chloro-ketone. When this emulsion was warmed to 60°, the chloro-ketone dissolved, and the chlorobenzene layer could readily be separated. On cooling, this layer deposited part of the desired product, and the remainder was obtained by removing two-thirds of the chlorobenzene under diminished pressure. The ketone was purified by distillation at 20 mm. and by recrystallisation from alcohol; b. p. 165°/20 mm., m. p. 64°.

The preparation of the *isonitrosoketone* met with great difficulties. Hartung and Munch's method (*loc. cit.*) gave a very small yield of an oily product; when sodium ethoxide was used to catalyse the reaction between the chloro-ketone and alkyl nitrite, a violent reaction occurred, but the main product was *p*-chlorobenzoic acid, m. p. 243°. Attempts to prepare the diketone, and from it the glyoxime by oxidation of the chloro-ketone with selenium dioxide, were also unsuccessful. Finally, the method of Semon and Damerell (" Organic Syntheses," Vol. 10) gave a small yield of the desired product and much unchanged chloro-ketone; the latter was recovered and worked up until sufficient of the oximino-ketone had been accumulated. *p*-Chlorophenyl *isonitroso-n*-amyl ketone melted at 42° after crystallisation from ligroin. Oximation gave a nearly quantitative yield of the glyoxime, which, when crystallised from alcohol, melted at 206°.

The *nickel* derivative, prepared in the usual manner, was brown and only moderately soluble in benzene. Recrystallisation from this solvent gave a product of m. p. 266° which was regarded as the α-form (Found : Ni, 10·7; Cl, 12·2. $C_{24}H_{28}O_4N_4Cl_2Ni$ requires Ni, 10·4; Cl, 12·5%). The mother-liquor when precipitated with ligroin gave a product of m. p. 243°, indicating that a lower-melting isomeride was present. The amount of this product was too small to permit of further fractionation.

Nickel NN-*Di-n-propyldithiocarbamate.*—20% Potassium hydroxide solution (1 mol.) was shaken with carbon disulphide (1 mol.), and di-*n*-propylamine added slowly with cooling. The solution was then added to an aqueous solution of nickel chloride (1 mol.) and sodium acetate (3 mols.). The greenish-black *nickel* complex was extracted with acetone and recrystallised from this solvent; m. p. 135° (Found : Ni, 14·0; *M*, ebullioscopic in benzene, 447, 456. $C_{14}H_{28}N_2S_4Ni$ requires Ni 14·3%; *M*, 411).

Nickel NN-*di-n-butyldithiocarbamate*, m. p. 91°, was similarly prepared from di-*n*-butylamine (Found : Ni, 12·7; *M*, ebullioscopic in benzene, 469, 454. $C_{18}H_{36}N_2S_4Ni$ requires Ni, 12·6%; *M*, 467).

Specimens of these dithiocarbamates were heated to 20° above the m. p. for 10 minutes. The products were dissolved in cold acetone and fractionally precipitated with water. None of the fractions showed any appreciable change in m. p.; hence a second form does not appear to be produced by fusion.

Determination of Dipole Moments.—The dielectric constants of benzene solutions of the nickel complexes were determined by a resonance method with the apparatus described by Sugden (J., 1933, 769). In Table II, *w* is the weight fraction of solute, *d* the density, and ε the dielectric constant of the solution, and P_2 the total polarisation calculated in the usual manner. Owing to the low solubility and the small amount available of some of the substances examined, the values of P_2 are subject to a rather large error, and no attempt has been made to extrapolate to infinite dilution before calculating the dipole moment. The deep colour of the solutions made it impossible to obtain accurate measurements of refractive index; the value of P_E was therefore calculated from the usual refraction constants for the Na-*D* line, and no allowance made for atom polarisation or for the contribution of the nickel atom to the distortion polarisation. This will partly compensate for the neglect to extrapolate to infinite dilution. The benzene used as solvent had $d_4^{25°}$ 0·8734, $ε_{25°}$ 2·273.

TABLE II.

Dipole moments in benzene at 25°.

Nickel glyoxime.	w.	d.	ε.	P_2.	P_E(calc.).	μ.	Mean.
Methyl-*n*-propyl (α-form)	0·02424	0·8810	2·294	120	82	1·35 }	1·4
,, ,, ,,	0·03130	0·8822	2·294	124	,,	1·42 }	
Methyl-*n*-propyl (β-form)	0·01812	0·8809	2·292	130	,,	1·52 }	1·5
,, ,, ,,	0·02049	0·8811	2·294	133	,,	1·57 }	
Methyl-*n*-butyl (α-form)	0·02089	0·8792	2·285	127	91	1·32 }	1·3
,, ,, ,,	0·03628	0·8833	2·293	126	,,	1·30 }	
Methyl-*n*-butyl (β-form)	0·01581	0·8790	2·285	129	,,	1·35 }	1·3
,, ,, ,,	0·03822	0·8844	2·296	128	,,	1·34 }	
Methylbenzyl (α-form)	0·01895	0·8795	2·285	148	113	1·30	1·3
Methylbenzyl (β-form)	0·01841	0·8790	2·288	166	,,	1·60 }	1·6
,, ,,	0·03042	0·8839	2·301	168	,,	1·63 }	
p-Chlorophenyl-*n*-butyl (α-form)	0·01425	0·8782	2·283	193	130	1·74 }	1·8
,, ,, ,, ,,	0·01460	0·8788	2·285	199	,,	1·82 }	

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138. The Configurations of the Disulphoxides of Thianthren.

By T. W. J. TAYLOR.

BERGMANN and TSCHUDNOWSKY (*Ber.*, 1932, **65**, 457) measured the molecular electric moments of the geometrically isomeric disulphoxides of thianthren and found the values 1·7 D for the α-compound (m. p. 284°) and 4·2 D for the β-isomeride (m. p. 249°); and they deduced that the former is the *trans*-disulphoxide, with the oxygen atoms lying on the opposite sides of the heterocyclic ring, and the latter the *cis*-compound. The same conclusion has been reached by Baw, Bennett, and Dearns (J., 1934, 680) in the basis of the physical properties of the compounds. Consideration of the possible space arrangements of these compounds shows that this conclusion is probably erroneous, and that the configurations should be reversed.

Thianthren itself has a molecular electric moment of 1·5 D (Bennett and Glasstone, J., 1934, 128; Smyth and Walls, *J. Chem. Physics*, 1933, **1**, 337, give 1·41 D), which, as has been pointed out, must arise from the fact that the molecule has a folded structure,

FIG. 1.
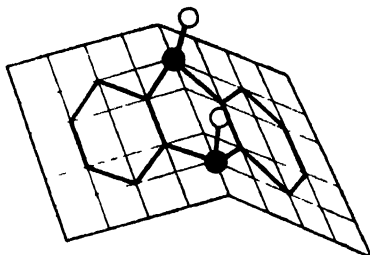
FIG. 2.
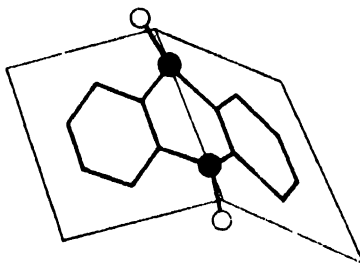
FIG. 3.
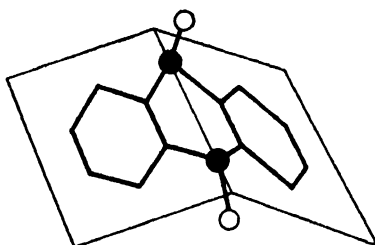
the folding taking place about a line passing through the sulphur atoms. It is very striking that the moment of the α-disulphoxide is only very slightly greater than that of the parent substance, in spite of the fact that the two oxygen atoms are united to the sulphur atoms by co-ordinate links (semipolar double bonds) each of which must possess a moment of about 2·5 D (Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **143**, 147). It follows that the space arrangement of the two S→O links in this compound must be such that their electric moments almost cancel each other.

Because of the folded structure of the ring system, oxygen atoms can be attached to the two sulphur atoms in three different ways (Baw, Bennett, and Dearns, *loc. cit.*). These are shown in the figures, in which the black spheres represent sulphur atoms and the others are oxygen atoms; the angles between the three covalencies of sulphur are taken as 110° in accordance with the majority of the evidence (Bennett and Glasstone, *loc. cit.*). Figs. 1 and 2 are both *cis*-arrangements, since in each the two oxygen atoms are on one side of the heterocyclic ring; they are capable of interconversion by bending about the line joining the sulphur atoms. Fig. 3 is the only possible *trans*-arrangement. Only two disulphoxides are known. It would thus appear that the α-disulphoxide with the small moment is the *cis*-compound (Fig. 2), and the β-compound is the *trans*-arrangement (Fig. 3). The other possible *cis*-arrangement (Fig. 1) would be expected to

have an electric moment of at least 6 D, since the component moments of the sulphoxide groups and the thianthren nucleus lie almost in the same direction. It is this configuration which is missing; the molecules appear to adopt the alternative *cis*-arrangement (Fig. 2).

This seems to be one of the few cases where, of two geometrical isomerides, the *cis*-compound has the greater symmetry, as is shown by its smaller electric moment and higher melting point.

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139. *The Densities of Aqueous Solutions of Potassium Acetate and Laurate.*

By C. R. BURY and G. A. PARRY.

THE work described here is a continuation of previous work (Davies and Bury, J., 1930, 2263) on the densities of soap solutions. Data for solutions of potassium acetate at 25° and for potassium laurate at 25° and 35° are presented, and it is shown that irregularities in the partial specific volumes of potassium acetate (Davies and Bury, *loc. cit.*) are due to experimental errors in the densities from which they were calculated. Further, an abrupt change in the density-composition curve of the laurate is discussed.

EXPERIMENTAL.

Acetic acid was distilled from chromium trioxide (Orton and Bradfield, J., 1924, **125**, 960), fractionally frozen three times, and then neutralised with pure potassium hydroxide. The resulting salt was twice recrystallised. A concentrated solution was prepared, and its strength determined by evaporation and conversion into the chloride. The more dilute solutions were prepared by dilution of this concentrated solution. A different preparation of the salt was used for each of the three series of density determinations.

Lauric acid was purified by two fractional distillations of its methyl ester under low pressure. Solutions of the potassium soap were prepared by treating a known weight of acid with the required quantity of carbon dioxide-free potassium hydroxide solution. This was prepared by washing sticks of caustic potash with water to remove the outer layers and then dissolving the cores. The entire operation was performed in resistance-glass vessels and in an atmosphere of nitrogen. The absence of carbonate in the alkali was proved by analysis by Winkler's method (Treadwell and Hall, "Analytical Chemistry," 1919, Vol. ii, 563). The strength of the most concentrated solution of each series was thus determined by synthesis, and the more dilute solutions were obtained from this by dilution. In making up the laurate solutions, analysing the acetate solutions, and diluting solutions, weights were corrected for buoyancy.

Dilute solutions of potassium laurate show a tendency to deposit acid soap : this tendency increases with the age and dilution of the solution and is favoured by low temperatures. No results are quoted for solutions which were cloudy or showed any other sign of the formation of acid soap.

In determining densities, Hartley and Barrett's procedure (J., 1911, **99**, 1072) was followed, except that flask-shaped pyknometers were used. Weights were standardised by Richards's method (*J. Amer. Chem. Soc.*, 1900, **22**, 144). The correction to which attention has been

Potassium acetate.

Series.	c, %.	$d_4^{25°}$.	Series.	c, %.	$d_4^{25°}$.	Series.	c, %.	$d_4^{25°}$.
2	62·30	·3453	1	44·67	1·2401	3	12·84	1·06150
1	61·56	·3417	2	41·71	1·2220	3	11·03	1·05233
3	60·82	·3373	3	39·78	1·2110	2	9·930	1·04649
2	57·25	·3149	1	35·26	1·1846	3	8·930	1·04148
3	55·68	·3060	2	29·89	1·1536	3	8·102	1·03733
3	54·51	·2992	1	29·01	1·1491	3	6·418	1·02883
1	53·13	·2909	2	25·02	1·1264	1	4·870	1·02111
2	50·59	·2749	3	24·86	1·1260	3	3·787	1·01575
2	49·05	·2655	1	18·60	1·09181	3	2·005	1·00686
3	46·91	·2533	2	15·01	1·07270	3	1·005	1·00204

Potassium laurate.

Series.	c, %.	$d_{4^\circ}^{25^\circ}$.	$d_{4^\circ}^{25^\circ}$.	Series.	c, %.	$d_{4^\circ}^{25^\circ}$.	$d_{4^\circ}^{25^\circ}$.
1	20·21	1·01514	1·01057	2	3·001	1·00016	0·99684
2	18·21	1·01351	1·00907	3	2·987	1·00015	0·99683
1	17·03	1·01247	1·00814	1	2·001	0·99927	0·99604
1	14·05	1·01000	1·00587	2	2·000	0·99927	0·99601
2	12·52	1·00861	1·00458	1	1·505	0·99883	0·99563
1	11·02	1·00740	1·00351	2	1·501	0·99881	0·99560
2	9·000	1·00550	1·00174	2	1·000	0·99835	0·99517
1	8·002	1·00470	1·00104	3	0·797	0·99813	0·99500
1	5·998	1·00289	0·99930	3	0·718	--	0·99491
1	4·006	1·00110	0·99774	3	0·643	–	0·99482
2	4·001	1·00105	0·99767	3	0·595	0·99789	0·99478
1	3·042	1·00021	0·99693	3	0·300	0·99749	0·99442

called by Grindley (J., 1928, 3297) was found negligible. The results obtained are in the tables, concentrations (c) being expressed as g. of salt per 100 g. of solution.

The error in determining densities is probably negligible in comparison with the uncertainty in the concentration of the solutions, except in the most dilute solutions. The uncertainty in the determination of the acetate solutions is probably about 0·05%. In the laurate solutions, the weight of lauric acid is known with accuracy; the uncertainty lies in the addition of the correct amount of alkali. Though all densities were determined to the fifth place, this fifth place is of no absolute value for the more concentrated solutions of potassium acetate owing to this uncertainty in the composition, and is therefore omitted from the tables. With potassium laurate the change of density with concentration is much smaller, and the measurements cover a smaller range of concentrations; consequently, the fifth place is probably significant even at the highest concentration studied.

DISCUSSION.

Our densities of potassium acetate solutions are slightly lower than those given in International Critical Tables (1928, Vol. iii, 90), based on determinations of previous investigators. The difference is 0·0007 at a concentration of 60%, and decreases with concentration, but not quite regularly. Partial specific volumes of potassium acetate calculated from the densities in the International Critical Tables had revealed some small irregularities (Davies and Bury, loc. cit., figure). The present work shows that these were due to small experimental errors, and that the density–composition and partial specific volume–composition graphs are smooth curves that show no sign of any abrupt change of slope or other irregularity.

The densities of a few solutions of potassium laurate were determined at 90° by Bunbury and Martin (J., 1914, **105**, 433), but these are not comparable with our results owing to difference of temperatures. Our results show that there is an abrupt change of slope in the density–composition graph similar to that found for potassium n-octoate. This graph consists of two almost straight lines which meet at a concentration of about 1%. It is not suggested that the slope of the curve changes discontinuously at this point (i.e., that the graph consists of two intersecting straight lines) but only that the slope changes rapidly over a narrow range of concentrations. The concentration at which the abrupt change of slope (the critical concentration for micelles) occurs is thus a somewhat ill-defined quantity, and various methods of plotting indicate slightly different values. It is, however, quite clear that the concentration at which the change occurs is lower at 35° than it is at 25°, the approximate concentrations being 0·8 and 0·9% respectively. From the measurements of McBain, Laing, and Titley (J., 1919, **115**, 1290; see also Randall, McBain, and White, J. Amer. Chem. Soc., 1926, **48**, 2517), there appears to be an abrupt change in the slope of the freezing point–composition curve at about the same concentration, but the data in this region are too scanty to fix the concentration with any accuracy.

Another feature of importance is the magnitude of the change of slope at this point. If concentrations are expressed as percentages, the slope of the density–composition curve for potassium laurate at 25° is 0·00133 in the range 0—0·8%, and 0·00090 for the

range 1·0—4·0%. The change of slope in the neighbourhood of 0·9% is therefore 0·00043. At 35° the change of slope is appreciably smaller (0·00035), and at higher temperatures the abrupt change of slope may be expected to become too small to be detectable.

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140. *Studies in Chelation. Part II. The Stabilisation of Kekulé Forms in* o-*Hydroxyacetophenones.*

By WILSON BAKER and (MISS) O. M. LOTHIAN. •

EVIDENCE was brought forward by Baker (J., 1934, 1684 •) that the formation of six-membered chelate rings containing co-ordinately linked hydrogen in o-hydroxyacetophen-ones was dependent upon the presence of a double bond between the carbon atoms bearing the hydroxyl and the acetyl group. It was shown that this accounted for (1) the difference in properties between 2 : 4- and 4 : 6-diacetylresorcinol, only the former of which behaved like a fully chelated compound, (2) the non-chelation of saturated β-hydroxyketones as compared with the known chelation of the unsaturated enolic forms of β-diketones, and (3) the abnormal formation of 2 : 4-diacetylresorcinol from 4-O-acetylresacetophenone by heating with aluminium chloride. It is evident that (1) and (3) involve the idea of a " fixed " (or largely fixed) Kekulé form in the aromatic nucleus, and in connexion with the present work it was essential to find a trustworthy means of detecting such a stable form.

In order to detect fixed Kekulé forms Mills and Nixon (J., 1930, 2510) utilised the fact that o-diazo-coupling, or o-bromination of p-substituted phenols, will occur on that side of the hydroxyl group which bears the double bond, and Baker (*loc. cit.*) similarly made use of the migration of an acetyl group from the phenolic oxygen atom to an o-carbon atom (Fries reaction). Objections may be raised to each of these methods when applied to o-hydroxyacetophenones; in particular, both bromine and aluminium chloride may prevent chelation by combining with the nuclear acetyl group (see Baker, *loc. cit.*, p. 1686).

The molecular rearrangement of the phenyl allyl ethers to give o-allylphenols appears to afford one of the best methods of establishing the position of the double bonds in the . nucleus. It is evident that the allyl group can migrate only to that o-carbon atom which is doubly bound to the C·O·CH₂·CH:CH₂ group, since, if we may assume the symmetrical arrangement of the double bonds in naphthalene, the facts that β-naphthyl allyl ether rearranges to 1-allyl-2-naphthol, and that the allyl ether of 1-allyl-2-naphthol will not rearrange at all (Claisen, *Ber.*, 1912, **45**, 3157), can only be interpreted in this sense (com-pare also the rearrangements of the O-allyl ethers of acetoacetic ester and acetylacetone; Claisen, *loc. cit.*). Again no reasonable mechanism of the reaction can be devised without assuming the participation of a double bond (see Ingold, *Ann. Reports*, 1926, 143). This rearrangement of the phenyl allyl ethers has been the subject of much study (Claisen, *loc. cit.*; Claisen and Eisleb, *Annalen*, 1913, **401**, 21; Claisen, Kremers, Roth, and Tietze, *ibid.*, 1925, **442**, 210; Claisen and Tietze, *ibid.*, 1926, **449**, 81; *Ber.*, 1925, **58**, 275; 1926, **59**, 2344; Hurd, Greengard, and Pilgrim, *J. Amer. Chem. Soc.*, 1930, **52**, 1700) and in connexion with the present work the following points may be noted : (1) the reaction, usually more or less exothermic, takes place when the allyl ethers are heated to about 200°, no catalyst or solvent being necessary, and thus any interference with the chelation between hydroxy and acetyl (or other chelating groups) is avoided; (2) the yields are generally satisfactory; (3) the reaction is free from the ambiguity as to which ortho-position is the most " active " in the ordinary sense of the word, a difficulty which may arise in all cases, except those few where the whole molecule is symmetrical about the phenolic group and the alternative positions are identical (*e.g.*, phenol itself, simple p-

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• This paper, entitled " A New Factor controlling Certain Chelations, with Special Reference to Disubstitution in the Resorcinol Nucleus," is to be regarded as Part I.

substituted phenols, etc.), where reactions such as bromination or diazo-coupling are employed; (4) the somewhat high temperatures involved, as compared with those employed in the other reactions cited, do not appear to be a disadvantage, since chelation is not affected, at least to any great extent, by considerable rise of temperature; indeed the abnormal boiling points of certain o-compounds as compared with the *m*- and *p*-isomerides—many well above 200°—afford, perhaps, the most important indication of chelation, and, further, the chelation of, for example, o-nitrophenol shows no sign of breaking down in presence of water at 200° (Sidgwick, Spurrell, and Davies, J., 1915, **107**, 1202).
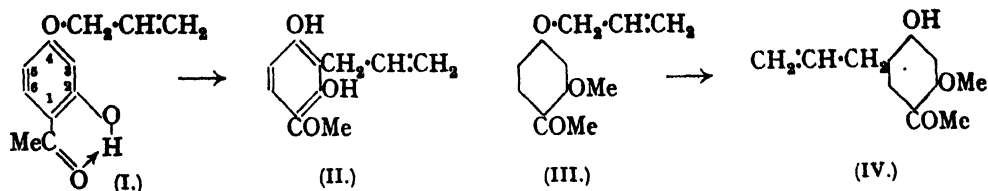
The present paper deals with the molecular rearrangement of 4-O-*allylresacetophenone* (I), and of 2-O-*methyl*-4-O-*allylresacetophenone* (III). Owing to chelation between the hydroxyl and the acetyl group in (I), the double bonds in the benzene nucleus should be stabilised as shown, and the allyl group should migrate to position 3, giving 3-*allylresaceto-phenone* (II). This expectation was realised, since the rearrangement of (I) gave (II) in not less than 85% yield, and no other definite product could be isolated. In 2-O-methyl-4-O-allylresacetophenone (III) chelation between the methoxyl and the acetyl group is impossible, no fixation of a Kekulé form will occur, and molecular rearrangement should give the usual symmetrical type of product, namely, 2-O-*methyl*-5-*allylresacetophenone* (IV). This prediction was again verified, since (IV) was produced from (III) in a yield of 60%, and no other individual product could be isolated. These results are entirely in harmony with the deductions drawn in Part I concerning the chelation between hydroxyl and acetyl. It may be noted that the electromeric effect MeO—C=C—C=O possible in (III) is apparently too weak to prevent the migration of the allyl group into the normal position 5.
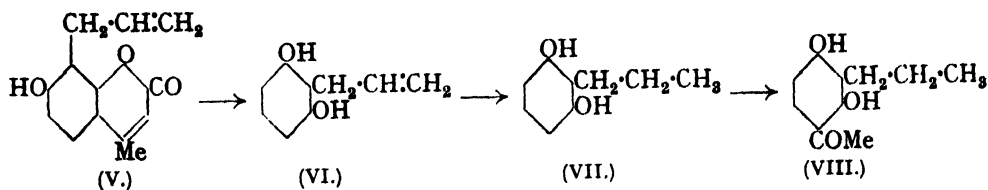
Compound (I) was prepared by direct allylation of resacetophenone, and methylation of (I) with methyl sulphate in acetone solution gave (III). These compounds were shown to be 4-O-allyl derivatives by the fact that (III) could also be obtained by the allylation of *iso*paeanol. The orientation of the allyl group in (II) was established in the following way. Catalytic reduction of (II) with hydrogen and palladium gave 3-n-*propylresaceto-phenone* (VIII), a compound which was then synthesised by an unambiguous method. 7-Hydroxy-4-methylcoumarin was converted into 7-*allyloxy*-4-*methylcoumarin*, and thence by the action of heat into 7-*hydroxy*-4-*methyl*-8-*allylcoumarin* (V), which when hydrolysed by boiling with aqueous sodium hydroxide yielded 2-*allylresorcinol* (VI) (compare Limaye, *Ber.*, 1932, **65**, 375; Baker, J., 1934, 1954). Catalytic reduction of (VI) gave 2-n-*propyl-resorcinol* (VII), which reacted with acetonitrile under the conditions of the Hoesch synthesis to give 3-n-propylresacetophenone (VIII), identical with that prepared by the catalytic reduction of (II). Owing to the reactivity of the allyl group it was found impossible to convert (VI) directly into (II) by the method either of Hoesch or of Nencki. The structures assigned to (V), (VI), and (VII) are established by the facts that both (VI) and (VII) differ widely in their properties from the known 4-allyl- and 4-n-propyl-resorcinols.

Methylation of (II) with methyl sulphate under ordinary conditions gives mainly

4-O-*methyl-3-allylresacetophenone* (IX), but in acetone solution the product is 3-*allylresacetophenone dimethyl ether* (X) (liquid, b. p. 169—170°/15 mm.). Methylation of (IV) gave the isomeric 5-*allylresacetophenone dimethyl ether* (XI) (m. p. 88—89°); the nonidentity of these two compounds establishes the position of the allyl group in (IV).

(IX.)

OMe
CH$_2$·CH:CH$_2$
OH
COMe

(X.)

OMe
CH$_2$·CH:CH$_2$
OMe
COMe

(XI.)

OMe
CH$_2$:CH·CH$_2$
OMe
COMe

(XII.)

OH
CH$_2$:CH·CH$_2$ CH$_2$·CH:CH$_2$
OH
COMe
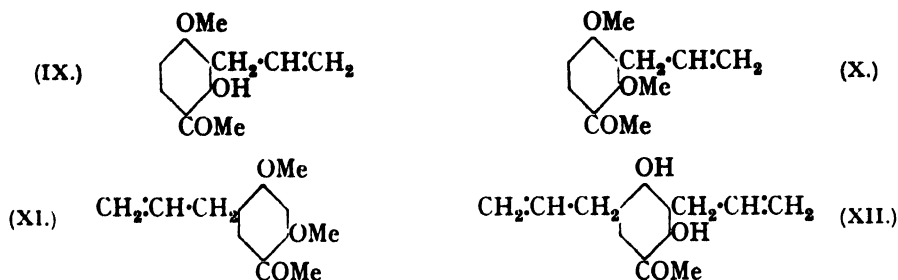
Allylation of (II) gave a monoallyl ether, 4-O-*allyl-3-allylresacetophenone*. If the fixation of the double bonds in this compound is complete, the normal rearrangement should not occur; the reaction was found to take place slowly (4 hours), and was not exothermic, an approximately 20% yield of crude 3 : 5-*diallylresacetophenone* (XII) being isolated. Allylation of (IV) gave 2-O-*methyl-4-O-allyl-5-allylresacetophenone*, which underwent rearrangement (slightly exothermic) to give 2-O-methyl-3 : 5-diallylresacetophenone (uncharacterised) (30% yield), which was directly methylated, yielding 3 : 5-*diallylresacetophenone dimethyl ether*. This same dimethyl ether was obtained by the methylation of (XII), the identity of the two specimens being established by a direct comparison of their crystalline *semicarbazones*, thus proving the constitutions assigned to (XII), 2-O-methyl-4-O-allyl-5-allylresacetophenone, and 3 : 5-diallylresacetophenone. These facts indicate that the fixation by chelation of the Kekulé forms in *o*-hydroxyacetophenones is not rigidly complete, although the rearrangement of (I) shows that the fixation must occur to a considerable extent.

Experimental.

4-O-*Allylresacetophenone* (I).—A mixture of resacetophenone (76 g.; 1 mol.), freshly ignited potassium carbonate (90 g.), and allyl bromide (61 g.; 1 mol.) in anhydrous acetone (180 c.c.) was refluxed and continuously stirred on the water-bath for 6 hours. Most of the acetone was now removed by distillation, and the remaining solution was acidified with dilute hydrochloric acid and extracted with ether. The pure product is best obtained by isolation as its very sparingly soluble sodium salt. The ethereal layer was shaken with excess of 2N-sodium hydroxide, and the precipitated sodium salt collected on a sintered glass funnel. Decomposition with dilute acid and extraction with ether yielded 4-O-*allylresacetophenone* (67 g.) as a faintly yellow liquid, b. p. 156—157°/9 mm. (Found : C, 68·9; H, 6·3. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·2%). It gives an intense brownish coloration with alcoholic ferric chloride.

2-O-*Methyl-4-O-allylresacetophenone* (III).—(A) The methylation of 4-O-allylresacetophenone could be satisfactorily accomplished only in acetone solution, owing to the feeble phenolic function of the hydroxyl group (compare Baker and Robinson, J., 1928, 3115). 4-O-Allylresacetophenone (5 g.) in acetone (150 c.c.) was methylated by the alternate addition of methyl sulphate (45 c.c.) and an excess of 20% aqueous potassium hydroxide in small quantities, the mixture being allowed to boil, and then shaken at frequent intervals during ½ hour. The alkaline liquor was diluted and extracted with ether and the extracts were shaken with 20% potassium hydroxide solution, dried, and distilled, leaving a faintly coloured oil, which solidified at 0°. 2-O-*Methyl-4-O-allylresacetophenone* distils unchanged at 171°/9 mm., and separates from light petroleum (b. p. 40—60°) at 0° in flaky irregular crystals, m. p. 31° (Found : C, 69·8; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). (B) *iso*Paeanol (1·5 g.) (Baker, J., 1934, 1691; compare Mauthner, *J. pr. Chem.*, 1933, 136, 208), allyl bromide (3 c.c.), acetone (25 c.c.), and potassium carbonate (5 g.) were heated on the steam-bath for 6 hours with continual stirring. After addition of dilute sodium hydroxide solution, ether extracted a colourless oil, which solidified at 0° and then melted at 28—29°. After crystallisation it melted at 31°, either alone or mixed with the specimen prepared as under (A).

3-*Allylresacetophenone* (II).—Pure 4-O-allylresacetophenone (2 g.) was heated cautiously

in an oil-bath, the temperatures both of the bath and of the substance being recorded. Rearrangement began at about 180° with evolution of heat and the tube was raised from the bath for a few minutes so that the temperature of the melt did not rise above 200°. Unless this precaution was taken, the highly exothermic rearrangement caused considerable rise of temperature, and profound decomposition of the product ensued. The temperature was then kept at 200—210° for 2¼ hours, and, on cooling, faintly coloured crystalline 3-allylresacetophenone (2 g.), m. p. 113—130°, was obtained. The powdered product, washed twice with cold light petroleum (b. p. 40—60°), lost 6% in weight and the melting point rose to 119—130°; the washings contained about 50% of 3-allylresacetophenone.

A similar rearrangement of 4-O-allylresacetophenone (5·9 g.) at 210—215° for 1¼ hours gave a product, which was fractionally crystallised from light petroleum (b. p. 80—100°). After several crystallisations there was isolated a total of 4·79 g. of pure 3-allylresacetophenone, m. p. 132—133° (80% yield). The mother-liquors contained a further small quantity of crude 3-allylresacetophenone, but no other crystalline substance could be obtained.

The results of these two experiments indicate that the molecular rearrangement of 4-O-allylresacetophenone gives certainly not less than an 85% yield of 3-allylresacetophenone. 3-*Allylresacetophenone* separates from benzene, dilute alcohol, or acetic acid in flat prisms, m. p. 133° (Found : C, 68·9; H, 6·3. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·2%). Addition of ferric chloride to its alcoholic solution gives an intense dull purplish-red colour.

4-O-*Methyl-3-allylresacetophenone* (IX).—3-Allylresacetophenone was methylated in 10% aqueous potassium hydroxide with methyl sulphate at about 30°, the mixture being finally heated on the steam-bath for ¼ hour. An ethereal extract yielded a solid, which separated from dilute acetic acid in colourless, compact, rhombic plates, m. p. 61° (Found : C, 69·9; H, 6·9. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). The substance gives an intense reddish-violet colour with alcoholic ferric chloride, and dissolves to a pale yellow solution in hot dilute aqueous sodium hydroxide.

3-*Allylresacetophenone Dimethyl Ether* (X).—3 Allylresacetophenone (1 g.) was treated in acetone (40 c.c.) with methyl sulphate (15 c.c.) and excess of 20% aqueous potassium hydroxide, as in the methylation of (I) (above). There was finally obtained a colourless oil, which was twice distilled in a vacuum; b. p. 169—170°/15 mm. (Found : C, 70·9; H, 7·3. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

7-*Allyloxy-4-methylcoumarin*.—A mixture of 7-hydroxy-4-methylcoumarin (88 g.; 1 mol.), allyl bromide (61 g.; 1 mol.), anhydrous potassium carbonate (100 g.), and acetone (300 c.c.) was stirred under reflux on the steam-bath for 6 hours. After removal of the acetone by distillation and addition of water, the colourless solid was collected, washed with dilute sodium hydroxide solution, then water, and dried (yield, 87 g.). The compound had m. p. 101°, unaltered by crystallisation from dilute acetic acid, from which it separated in prismatic needles (Found : C, 72·1; H, 5·6. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·5%).

7-*Hydroxy-4-methyl-8-allylcoumarin* (V).—The preceding compound was heated in an oil-bath in quantities of 5 g., the precaution described in the molecular rearrangement of (1) being taken. After the exothermic reaction, which took place at about 240°, the product was kept at 210° for 1¼ hours; the crude product thus obtained melted at 165—175°. 7-*Hydroxy-4-methyl-8-allylcoumarin* separated from alcohol in small compact bi-pyramids, m. p. 193—194° (Found : C, 72·1; H, 5·7. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·5%). Its alcoholic solution shows a weak blue fluorescence, and gives no coloration with ferric chloride. The solution in concentrated sulphuric acid is pale yellow and possesses a strong blue fluorescence.

2-*Allylresorcinol* (VI).—7-Hydroxy-4-methyl-8-allylcoumarin (5 g.) was heated on the steam-bath for 4 hours with 20% aqueous sodium hydroxide (35 c.c.) in an atmosphere of coal gas. The liquid was acidified, and yielded to ether a light brown oil, which solidified on cooling. This was distilled, and the fraction, b. p. 155—160°/11 mm., recrystallised from light petroleum (b. p. 40—60°). It formed colourless prismatic needles, m. p. 53° (Found : C, 71·5; H, 6·6. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%). It was easily soluble in water, and the cold aqueous solution gave an indigo-blue colour with a trace of ferric chloride; if the mixture was kept or gently warmed, the blue colour faded and an insoluble reddish oxidation product separated. 2-*Allylresorcinol* gives no coloration with alcoholic ferric chloride (the isomeric 4-allylresorcinol is a liquid, b. p. 144—146°/5 mm.; Hurd, Greengard, and Pilgrim, *loc. cit.*).

2-*Propylresorcinol* (VII).—2-Allylresorcinol (3·5 g.) was reduced in alcohol (20 c.c.) with hydrogen in presence of palladium chloride (0·2 g.) at room temperature; the theoretical absorption of hydrogen took place in 2 hours. After filtration, the alcohol on evaporation left a colourless solid (m. p. 90—95°), which separated from benzene in flat lustrous prisms, m. p.

106° (Found : C, 70·9; H, 7·9. $C_9H_{12}O_2$ requires C, 71·1; H, 7·9%). 2-*Propylresorcinol* is easily soluble in water, and its behaviour towards aqueous or alcoholic ferric chloride is identical with that of 2-allylresorcinol. The fluorescein reaction leads to a cherry-red solution exhibiting a weak green fluorescence (compare Crabtree and Robinson, J., 1918, 113, 869) (the isomeric 4-*n*-propylresorcinol has m. p. 81—82°, and its aqueous solution gives a red-violet coloration with ferric chloride).

3-n-*Propylresacetophenone* (VIII).—(A) A mixture of 2-propylresorcinol (1 g.), acetonitrile (2 c.c.; distilled over phosphoric oxide), dry ether (20 c.c.), and powdered anhydrous zinc chloride (1 g.) was saturated with hydrogen chloride at 0°. After 24 hours, fresh dry ether was added; after shaking, it was decanted from the ketimine hydrochloride, which was hydrolysed by heating on the water-bath for ¼ hour. The ketone (1·1 g.; m. p. 124—126°) which separated was crystallised from 50% alcohol and then from light petroleum (b. p. 80—100°) and obtained as small prismatic needles, m. p. 127—128° (Found : C, 67·9; H, 7·2. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%). 3-n-*Propylresacetophenone* gives a dull reddish-brown colour with ferric chloride, and sublimes slowly at 100°. (B) 3-Allylresacetophenone (5 g.) was reduced in alcohol (25 c.c.) with hydrogen in presence of palladium chloride (0·4 g.). Theoretical absorption of hydrogen took place in 1 hour, and evaporation of the filtered solution left a colourless solid; crystallisation from 50% alcohol gave lustrous hexagonal plates, m. p. 127—128°, which was not depressed on admixture with the substance prepared by method (A) (Found in material dried at 100° in a vacuum over phosphoric oxide : C, 67·9; H, 7·2%).*

2-O-*Methyl-5-allylresacetophenone* (IV).—Pure 2-O-methyl-4-O-allylresacetophenone (III) (5 g.) was heated (oil-bath at 215°) for ¾ hour, the maximum temperature reached by the melt being 218°. On cooling, a semi-solid, light reddish-violet mass was obtained, which was shaken with excess of 10% aqueous sodium hydroxide and ether. The ethereal layer yielded unchanged material (III) (1 g.), and the alkaline layer on acidification gave crude 2-O-*methyl-5-allylresacetophenone* (4·0 g.). Recrystallisation from a small volume of benzene gave a slightly coloured product (2·4 g.), m. p. 135° with slight previous softening; yield, 60%. It separated from benzene in minute prisms, or from very dilute acetic acid in branching fern-like aggregates, m. p. 136° (Found in material dried over sodium hydroxide in a vacuum at 100° : C, 69·7, 69·8; H, 6·9, 6·6. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). The benzene mother-liquors left a dark oil, which yielded a further very small quantity of 2-O-methyl-5-allylresacetophenone, but no other crystalline material could be isolated. The substance gives no coloration with alcoholic ferric chloride, but is freely soluble in cold aqueous sodium hydroxide.

5-*Allylresacetophenone Dimethyl Ether* (XI).—The foregoing compound, after treatment with aqueous potassium hydroxide and methyl sulphate in the usual way, yielded to ether a colourless solid, which separated from light petroleum (b. p. 60—80°) in irregular prisms, m. p. 88—89° (Found : C, 70·9; H, 7·5. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

4-O-*Allyl-3-allylresacetophenone*.—3-Allylresacetophenone (II) (4 g.) in acetone (100 c.c.) was stirred under reflux at the boiling point for 6 hours with allyl bromide (2·5 g.) and potassium carbonate (12 g.). After removal of the acetone and addition of dilute hydrochloric acid the product was extracted with ether and the extracts were shaken with 8% sodium hydroxide solution, dried, and distilled, leaving an oil, which solidified on cooling (3 g.). It separated at 0° from light petroleum, in which it was rather easily soluble, in needles, m. p. 34·5° (Found : C, 72·2; H, 6·9. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). The compound is weakly phenolic, being extracted from dilute alkaline solutions by ether, but its alcoholic solution gives a deep purplish colour with ferric chloride.

3 : 5-*Diallylresacetophenone* (XII).—4-O-Allyl-3-allylresacetophenone (1·5 g.) was heated for 6 hours at 210°, and the resulting dark pasty product was crystallised successively from light petroleum (b. p. 60—80°), dilute alcohol, and light petroleum, yielding 0·3 g. of colourless prisms, m. p. 89—90° (Found : C, 72·7; H, 7·3. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%).

2-O-*Methyl-4-O-allyl-5-allylresacetophenone*.—This substance was prepared by allylation of 2-O-methyl-5-allylresacetophenone (IV) (3·4 g.) in the usual way with allyl bromide (3·4 g.), potassium carbonate, and acetone (20 c.c.) for 5 hours, and subsequent dilution (yield, 3·8 g.). It separated from alcohol in long needles, m. p. 79° (Found : C, 73·2; H, 7·4. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·4%).

3 : 5-*Diallylresacetophenone Dimethyl Ether*.—(A) The preceding compound (2 g.) was heated

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* The orientation of 3-*n*-propylresacetophenone establishes the correctness of the formula assigned to a product, m. p. 108—109°, obtained by Rosenmund, Buchwald, and Deligiannis (*Arch. Pharm.*, 1933, 271, 344) and regarded as 5-*n*-propylresacetophenone.

for $\frac{1}{4}$ hour at 210° (maximum temperature of the melt, 213°), and then shaken with ether and 8% sodium hydroxide solution. The ethereal layer yielded unchanged material (1 g.), and the alkaline layer was treated with excess of methyl sulphate and alkali, yielding an oil (0·3 g.), which distilled at 178—179°/13 mm. (Found: C, 73·9; H, 7·6. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%). (B) 3 : 5-Diallylresacetophenone (XII), when treated with excess of methyl sulphate and alkali in acetone, gave the dimethyl ether, b. p. 178—179°/13 mm. (Found: C, 73·7; H, 7·6%). These products were separately treated with semicarbazide hydrochloride and sodium acetate in dilute alcoholic solution at 60° for 20 minutes; after crystallisation from benzene the two specimens of the *semicarbazone*, minute needles, melted at 135—136°, either alone or mixed (Found: N, 13·4. $C_{17}H_{23}O_3N_3$ requires N, 13·3%).

The authors' thanks are due to the Chemical Society for a grant.

141. *The Constituents of Natural Phenolic Resins. Part I. Matairesinol.*

By ROBERT D. HAWORTH and THOMAS RICHARDSON.

SINCE Schroeter, Lichtenstadt, and Irineu (*Ber.*, 1918, **51**, 1587) suggested that guaiaretic acid was an αδ-diarylbutane derivative of skeletal formula (I), other naturally occurring compounds such as podophyllin (Borsche and collaborators, *Annalen*, 1932, **494**, 126; 1932, **499**, 59; 1933, **502**, 264; Spath and collaborators, *Ber.*, 1932, **65**, 1526, 1773; 1933, **66**, 125), sulphite-liquors lactone or tsugaresinol (Holmberg, *Ber.*, 1921, **54**, 2389, 2406; *Ann. Acad. Sci. Fennicæ*, 1927, A, **29**, No. 6; Erdtman, *Annalen*, 1934, **513**, 229; Kawamura, *Bull. Imp. Forestry Exp. Stat. Tokyo*, 1932, **31**, 73; Emde and Schartner, *Naturwiss.*, 1934, **44**, 734), and olivil (Vanzetti and Dreyfuss, *Gazzetta*, 1934, **64**, 381) have been recognised as belonging either to this class (I) or to its cyclised 1-phenylnaphthalene form (II). It had been anticipated (see Meyer and Jacobson, " Lehrbuch der Organischen Chemie," vol. II, part IV, p. 166) that a reinvestigation of pinoresinol, lariciresinol, and matairesinol would probably reveal a close relationship between these compounds and guaiaretic acid, and while the present work was in progress Erdtman (*Svensk Kem. Tidskr.*, 1934, **46**, 229) showed that pinoresinol is a C_{20} compound of type (I) and not a C_{19} compound as earlier workers (Bamberger and co-workers, *Monatsh.*, 1894, **15**, 505; 1897, **18**, 481; 1900, **21**, 949; 1917, **39**, 474; Zincke, Erben, and Jele, *ibid.*, 1924, **44**, 571) suggested. Further Erdtman (*loc. cit.*) suggests that pinoresinol dimethyl ether and eudesmin (Robinson and Smith, *J. Proc. Roy. Soc. N.S. Wales*, 1915, **48**, 449) are optical antipodes.
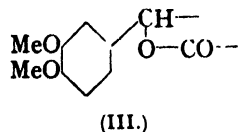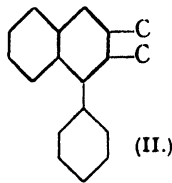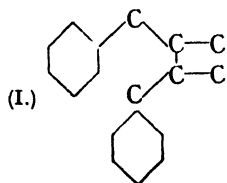
Structures (I) and (II) are derivable from two molecules of allylbenzene by dimerisation at the β-carbon atoms. With the exception of podophyllin, the natural products mentioned above are related to eugenol and it is probable that cubebin (Mameli, *Gazzetta*, 1907, **37**, ii, 483; 1909, **39**, i, 477, 494; 1912, **42**, ii, 546, 551; 1921, **51**, ii, 353), hinokinin (Yoshiki and Ishiguro, *J. Pharm. Soc. Japan*, 1933, **53**, 11), and sesamin (Bertram, Steur, and Watermann, *Biochem. Z.*, 1928, **197**, 1; Böeseken and Cohen, *ibid.*, 1928, **201**, 454) represent the safrole analogues.

The present communication describes an investigation on the structure of matairesinol, which was isolated by Easterfield and Bee (J., 1910, **95**, 1028) from the heart-wood of the matai (*Podocarpus spicatus*), a tree growing in the forests of New Zealand. Easterfield

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and Bee proposed the formula $C_{19}H_{20}O_6$, and suggested a relationship with pinoresinol and lariciresinol (Bamberger and co-workers, *Monatsh.*, 1897, **18**, 500; 1899, **20**, 647, 755; 1900, **21**, 564; 1903, **24**, 249; 1917, **38**, 470). They established the presence of a lactone group and two methoxyl groups, and the occurrence of two phenolic hydroxyl groups was indicated by the ferric reaction and the preparation of a dibenzoyl derivative. The matairesinol used in the present research was isolated and purified as described by Easterfield and Bee. No discrepancy in melting point was observed, but the specific rotation was $- 48.6°$ and not $- 4.89°$ as reported by the previous workers. The analytical figures now obtained suggest the formula $C_{20}H_{22}O_6$, and this is fully confirmed by an examination of the derivatives of matairesinol.

Matairesinol dimethyl ether, $C_{22}H_{26}O_6$, is a saturated lævorotatory lactone, which is oxidised by potassium permanganate to veratric acid in yields exceeding 50% of the theoretical. This result suggests that matairesinol dimethyl ether contains two veratryl radicals, and this view is confirmed by the ready conversion of the ether into *dibromo-* and *dinitro-*derivatives, $C_{22}H_{24}O_6Br_2$ and $C_{22}H_{24}O_{10}N_2$ respectively. If one of the α-carbon atoms is involved in the lactone group as indicated by the partial formula (III), 4 : 5-dinitro-veratrole and trinitroveratrole should be obtained from the dimethyl ether by the action of boiling 50% nitric acid and cold fuming nitric acid respectively. Actually, the former reagent yielded the dinitro-derivative, $C_{22}H_{24}O_{10}N_2$, mentioned above, and the latter reagent gave a strongly lævorotatory *tetranitro-*derivative, $C_{22}H_{22}O_{14}N_4$.

Oxidation of matairesinol dimethyl ether with lead tetra-acetate gave a crystalline oxidation product in yields varying between 10 and 15%. This was resolved by fractional crystallisation into the *lactone* of 6 : 7-*dimethoxy-1-(3' : 4'-dimethoxyphenyl)-3-hydroxy-methylnaphthalene-2-carboxylic acid* (IV) and the isomeric *lactone* of 6 : 7-*dimethoxy-1-(3' : 4'-dimethoxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic acid* (V). The structure assigned to these lactones depends upon experiments described in the following communication, and the identification of these two oxidation products leads directly to the formula (VI ; R = Me) for matairesinol dimethyl ether. This structure is in complete agreement with the observed properties of the ether. Dimroth and Schweizer (*Ber.*, 1923, **56**, 1375) showed that toluene was oxidised to benzyl alcohol by means of lead tetra-acetate, and this observation, together with the well-established reactivity of the 6-position of the veratrole nucleus, provides a reasonable explanation of the action of lead tetra-acetate on matairesinol dimethyl ether.

(IV.)   (V.)   (VI.)
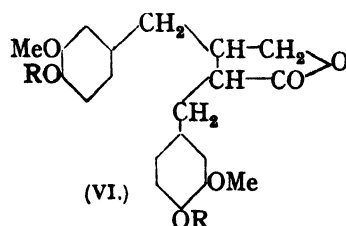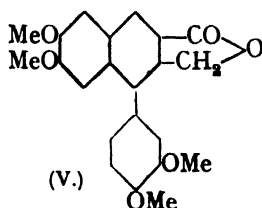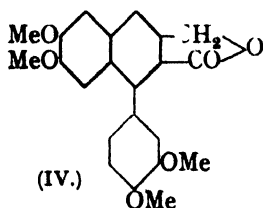
The positions of the phenolic hydroxyl groups in matairesinol have been determined by oxidising the *diethyl* ether with potassium permanganate. As 3-methoxy-4-ethoxy-benzoic acid was isolated in yields greater than 50% of the theoretical, matairesinol must have the formula (VI ; R = H).

Experiments concerned with the synthesis of matairesinol and similar compounds are in progress.

EXPERIMENTAL.

The resin (50 g.), obtained from heart shakes of adult matai trees growing on pumiceous soil at an altitude approximately 1800 feet above sea level, was boiled with methylated spirits (250 c.c.), and the hot solution filtered from chips of wood. On cooling, matairesinol (25 g.) separated in slender prisms, m. p. 74—76°, which contained alcohol of crystallisation. Re-crystallisation from 30% acetic acid yielded the anhydrous form in stout prisms, m. p. 117—118° (Found : C, 67.3, 67.1, 67.0 ; H, 6.3, 6.2, 6.3. Calc. for $C_{20}H_{22}O_6$: C, 67.0 ; H, 6.2%). In acetone (*c*, 2.409) $[\alpha]_D^{18}$ — 48.6°.

Matairesinol Dimethyl Ether.—Methyl sulphate (15 g.) was added to a solution of matairesinol (5 g.) in 4% methyl-alcoholic potassium hydroxide (50 c.c.). The solution was boiled and 50% aqueous potassium hydroxide was slowly added to maintain slight alkalinity. The methyl alcohol was removed, dilute sulphuric acid added to the residue, and the mixture boiled for 5 minutes. The *dimethyl* ether crystallised from methyl alcohol in stout prisms (4·8 g.), m. p. 127—128° (Found : C, 68·2, 68·1; H, 6·7, 6·8. $C_{20}H_{24}O_6$ requires C, 68·4; H, 6·7%). In chloroform (c, 3·740) it has $[\alpha]_D^{19°}$ − 35·6°. The elevated temperature in the methylation did not induce racemisation and an identical product was obtained by methylating the resinol at 15°. The ether dissolved in concentrated sulphuric acid to a blue-green solution, which turned brown on the addition of a drop of concentrated nitric acid. The lactone ring was opened slowly on boiling with dilute sodium hydroxide solution, but rapid hydrolysis occurred with warm methyl-alcoholic potassium hydroxide. The methyl ether was recovered, unchanged in m. p. and specific rotation, after treatment with hydrogen in the presence of a palladised carbon catalyst which was capable of reducing guaiaretic acid dimethyl ether.

Dibromomatairesinol dimethyl ether, prepared in 80% yield by the action of bromine (2·2 mols.) on a cold acetic acid solution (10 parts) of the ether, crystallised from alcohol in long prisms, m. p. 126—127° (Found : C, 48·6, 48·5; H, 4·7, 4·6. $C_{20}H_{22}O_6Br_2$ requires C, 48·5; H, 4·5%). The dibromo-compound, which does not decolorise bromine in chloroform solution, dissolves in concentrated sulphuric acid to a light brown solution, which becomes bright red on the addition of a drop of concentrated nitric acid. In chloroform (c, 3·540), it has $[\alpha]_D^{19°}$ − 38·4°.

Dinitromatairesinol dimethyl ether, prepared quantitively by the action of concentrated nitric acid (2·2 mols.) on a cold solution of the ether in glacial acetic acid (20 parts), crystallised from alcohol–chloroform in pale yellow needles, m. p. 179—180° (Found : C, 55·2, 55·1; H, 5·0, 5·1. $C_{20}H_{22}O_{10}N_2$ requires C, 55·4; H, 5·0%). In chloroform (c, 3·610) it has $[\alpha]_D^{19°}$ − 126·6°. It gives with concentrated sulphuric acid a bright red solution, which darkens on the addition of a drop of concentrated nitric acid. The dinitro-compound was reduced in alcoholic suspension with zinc dust and concentrated hydrochloric acid; the filtered solution gave a deep blue-green coloration with ferric chloride. This dinitro-compound was also obtained in 50% yield by boiling matairesinol dimethyl ether (1 part) with a mixture of concentrated nitric acid (10 vols.) and water (10 vols.) for 12 hours. When matairesinol dimethyl ether (1 part) was treated either with cold fuming nitric acid (15 vols.) or with boiling concentrated nitric acid (10 vols.) for 10 minutes, it was converted into a *tetranitro*-derivative, which crystallised from alcohol–acetone in colourless needles, m. p. 202—203° (Found : C, 46·5; H, 4·2. $C_{20}H_{20}O_{14}N_4$ requires C, 46·5; H, 4·2%). In acetone (c, 0·5260) it has $[\alpha]_D^{19°}$ − 161·6°.

Matairesinol diethyl ether, prepared by ethylating the resinol with ethyl sulphate in alcoholic solution as described in the preparation of the dimethyl ether, crystallised from methyl alcohol in colourless prisms, m. p. 97—98° (Found : C, 69·4; H, 7·6. $C_{24}H_{30}O_6$ requires C, 69·6; H, 7·3%).

Oxidation of the Ethers with Potassium Permanganate.—(a) A solution of matairesinol dimethyl ether (2 g.) in hot methyl alcohol (20 c.c.) was treated with 10% sodium hydroxide solution (4 c.c.). After boiling for 10 minutes, water (40 c.c.) was added, the alcohol removed, and the cooled solution subjected to a continuous stream of carbon dioxide during the gradual addition of 3% potassium permanganate solution (200 c.c.). The manganese dioxide was removed, and the concentrated filtrate acidified, boiled for 5 minutes, and extracted with chloroform. The extract, after being washed with sodium bicarbonate solution, yielded 0·2 g. of unchanged matairesinol dimethyl ether. Acidification of the bicarbonate solution gave a crude acid (1·3 g.), which yielded veratric acid (1·0 g.), m. p. 178—180° after crystallisation from hot water.

(b) A similar oxidation of the diethyl ether (2·0 g.) gave 0·2 g. of unchanged ether and 1·1 g. of 3-methoxy-4-ethoxybenzoic acid, m. p. 194°.

Oxidation of the Dimethyl Ether with Lead Tetra-acetate.—Matairesinol dimethyl ether (0·5 g.) in acetic acid (5 c.c.) was treated at 70° with lead tetra-acetate (1·2 g.) in acetic acid (15 c.c.). After heating for 10 minutes at 70°, water was added and the mixture was extracted with chloroform. The extract was washed with sodium bicarbonate solution, and the solvent removed; the residue solidified on trituration with a little methyl alcohol. The solid (0·5—0·8 g.), melting indefinitely between 190° and 215°, was dissolved in hot methyl alcohol–chloroform (7 : 3); the crystals, m. p. 237—241°, obtained on cooling were collected (A) and recrystallised several times from methyl alcohol–chloroform, giving colourless prisms, m. p. 250—252° (Found : C, 69·3; H, 5·5. $C_{20}H_{20}O_6$ requires C, 69·5; H, 5·3%), which were identified as (IV) by comparison with a specimen prepared as described in Part II. The chloroform was removed from the mother-liquors (A), and, on cooling, crystals, m. p. 200—203°, separated; after several

recrystallisations from methyl alcohol (carbon), slender prisms, m. p. 213—215° (Found: C, 69·4; H, 5·4. C₃₃H₃₀O₄ requires C, 69·5; H, 5·3%), were obtained, which were identified as (V) by comparison with a specimen prepared as described in Part II.

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142. *The Constituents of Natural Phenolic Resins. Part II.*
" Sulphite-liquors Lactone."

By ROBERT D. HAWORTH and GEORGE SHELDRICK.

IN view of the wide occurrence of compounds of the diarylbutane and phenylnaphthalene types (see preceding paper) methods for their preparation have been investigated. This communication concerns the synthesis of some substances of importance in connexion with the constitution of matairesinol and " sulphite-liquors lactone " (see Part I for the more important references).

Holmberg (*loc. cit.*) formulated " sulphite-liquors lactone " as a *cyclo*butane derivative, but the later investigations of Erdtman (*loc. cit.*) led to formula (I; R = H) or (II; R = H). Emde and Schartner (*loc. cit.*) identified " sulphite-liquors lactone " with the main constituent of the resin of *Picea excelsa*, and also with tsugaresinol which had been isolated previously by Kawamura (*loc. cit.*) from the wood of *Tsuga Sieboldii*, Carr. As a result of their analytical figures, Emde and Schartner suggest structure (III; R = H) for " sulphite-liquors lactone." Erdtman's conclusions are largely based on the isolation of veratroylveratric acid and 6 : 7-*dimethoxy*-1-(3'*:* 4'-*dimethoxyphenyl*)*naphthalene*-2 : 3-*dicarboxylic acid* (IV) as oxidation products of the dimethyl ether of the lactone. The formation of (IV) established the carbon skeleton of the dimethyl ether, and the positions of

(I.)   (II.)   (III.)
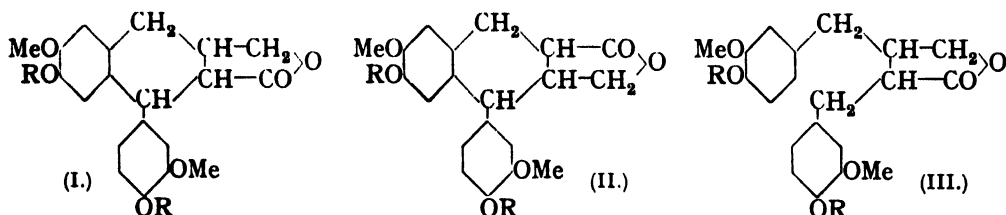
the phenolic hydroxyl groups were assumed from biogenetic relationships. The structure assigned to the acid (IV) depended on its identity with a synthetic acid, prepared by one of us and Dr. C. R. Mavin in May, 1932, by the dimerisation of 3 : 4-dimethoxyphenylpropiolic acid with acetic anhydride. The evidence in support of the structure rested entirely on analogy; phenylpropiolic acid is converted into 1-phenylnaphthalene-2 : 3-dicarboxylic acid (Michael, *Ber.*, 1912, **39**, 1909; Stobbe, *ibid.*, 1913, **40**, 3373) under similar conditions. During the present work conclusive evidence has been obtained for the structure of the acid (IV), the positions of the phenolic hydroxyl groups of " sulphite-liquors lactone " have been established, and a decision between (I), (II), and (III) has been made in favour of (II).

The *anhydride* of the dicarboxylic acid (IV) was decarboxylated by heating with quinoline and copper bronze to 6 : 7-*dimethoxy*-1-(3' : 4'-*dimethoxyphenyl*)*naphthalene* (V), but in very small yield. Fortunately, two additional methods were discovered for the preparation of (V), and its structure has been confirmed by demethylation, and distillation of the tetrahydroxy-compound with zinc dust, 1-phenylnaphthalene being obtained.

The first synthetical experiments were made with β-3 : 4-*dimethoxybenzoyl*-α-3' : 4'-

dimethoxybenzylidenepropionic acid (VI), the *γ-lactone* of which was obtained from veratraldehyde and sodium β-3 : 4-dimethoxybenzoylpropionate by the method of Borsche (*Ber.*,

MeO CO₂H
MeO CO₂H
(IV.) OMe OMe

MeO
MeO
(V) OMe OMe

MeO CO CH₂
MeO CH C·CO₂H
(VI.) OMe OMe
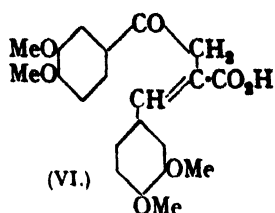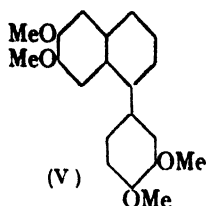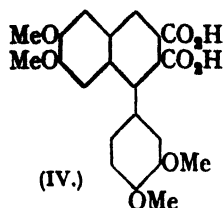
1914, **47**, 1108), the modifications introduced by Haq, Kapur, and Ray (J., 1933, 1087) giving inferior results. When the acid (VI) was heated with methyl-alcoholic hydrogen chloride, it was converted into the *methyl* ester of 6 : 7-*dimethoxy*-1-(3′ : 4′-*dimethoxyphenyl*)-*naphthalene-3-carboxylic acid*, from which the corresponding *acid* (VII) was prepared. This acid was also obtained by the action of alcoholic iodine on the lactone of (VI). The acid (VII) was converted into (V) in good yield by heating with quinoline and copper bronze. The difficulty experienced in attempts to esterify or reduce the acid (VI) has led to the examination of other routes to compounds of the diarylbutane and phenylnaphthalene types.

3 : 4 : 3′ : 4′-Tetramethoxybenzophenone reacted with ethyl succinate in the presence of potassium ethoxide to give *γ-di*-(3 : 4-*dimethoxyphenyl*)*itaconic acid* (VIII), the *anhydride* of which was converted into 1-*keto*-5 : 6-*dimethoxy*-3-(3′ : 4′-*dimethoxyphenyl*)*indene-2-acetic acid* (IX) by treatment with aluminium chloride. Stobbe and Vieweg (*Ber.*, 1902, **35**, 1727) showed that diphenylitaconic acid was converted into an orange indone derivative on treatment with cold sulphuric acid, and the bright red colour of (IX) is consistent with the suggested structure. Catalytic reduction of the indone (IX) gave an unusual result; both the keto-group and the ethylenic linkage were reduced and 5 : 6-*dimethoxy*-3-(3′ : 4′-*dimethoxyphenyl*)*hydrindene-2-acetic acid* was obtained. The substituted diphenylitaconic acid (VIII) was reduced catalytically to *bis*-(3 : 4-*dimethoxyphenyl*)*methylsuccinic acid* (X), but almost quantitative yields of this acid were obtained by condensing two molecular proportions of veratrole with ethyl hydroxymethylenesuccinate in cold acetic acid–sulphuric acid solution. The anhydride of (X), when treated with aluminium chloride in nitrobenzene, was converted in 90% yield into 4-*keto*-6 : 7-*dimethoxy*-1-(3′ : 4′-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene-2-carboxylic acid* (XI). The constitution was established by reducing the acid (XI), or better its *ethyl* ester, by Clemmensen's method to 6 : 7-*dimethoxy*-1-(3′ : 4′-*dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydronaphthalene-2-carboxylic acid*, which was converted into 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)naphthalene (V) by heating with selenium at 280°.

MeO CO₂H
MeO
(VII.) OMe OMe

MeO CH₂·CO₂H
MeO C·CO₂H
(VIII.) OMe OMe

MeO CH₂·CO₂H
MeO C
MeO CO
(IX.) OMe
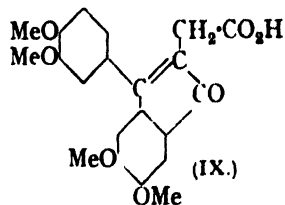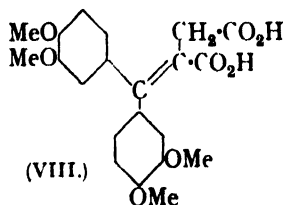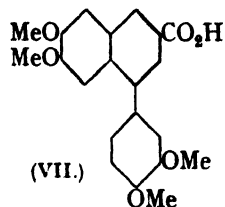
The accessibility of the acid (XI) rendered it extremely promising for the synthesis of compounds of type (I; R = Me). A dibromo-compound, probably *ethyl 3-bromo-4-keto-6 : 7-dimethoxy-1-(6′-bromo-3′ : 4′-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate*, was prepared by the action of bromine on the ethyl ester of (XI). The dibromo-compound was heated with diethylaniline and converted into *ethyl 4-hydroxy-6 : 7-dimethoxy-1-(6′-bromo-3′ : 4′-dimethoxyphenyl)naphthalene-2-carboxylate* (XII), which reacted with formaldehyde to give the *lactone of 4-hydroxy-6 : 7-dimethoxy-1-(6′-bromo-3′ : 4′-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid* (XIII), but the

difficulty experienced in the removal of the bromine from both the ester (XII) and the lactone (XIII) led to the temporary abandonment of this method.

MeO / MeO — CH$_2$·CO$_2$H / CH·CO$_2$H ... CH ... OMe ... OMe   (X.)

MeO / MeO — CO / CH$_2$ / CH·CO$_2$H ... CH ... OMe ... OMe   (XI.)

OH ... MeO / MeO ... CO$_2$Et ... Br ... OMe ... OMe   (XII.)
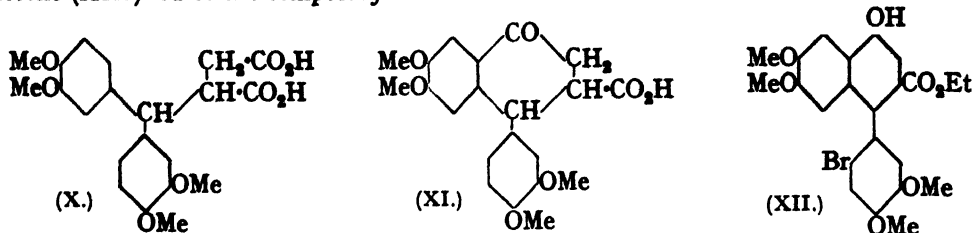
The ethyl ester of the acid (XI) reacted with ethyl formate in presence of sodium to give an almost quantitative yield of *ethyl 3-aldehydo-4-keto-6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate* (XIV), which was reduced with sodium amalgam to an acid, C$_{22}$H$_{26}$O$_8$, which is provisionally regarded as *4-hydroxy-6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid* (XV). The analytical figures obtained were in accordance with the suggested structure, but boiling with 10% sulphuric acid or heating at 200° converted the acid (XV), in 45% yield, into the α-form of the *lactone of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid* (I ; R = Me), m. p. 187°. This lactone can exist in a number of stereoisomeric forms, and the compound, m. p. 187°, is referred to as the α-form in order to distinguish it from a stereoisomeride which is described below. The explanation of this reductive lactonisation of (XV) into (I ; R = Me) must be deferred until more data are available, but the structure of the product is consistent with the properties. The lactone (I ; R = Me) reacted as a saturated compound towards both hydrogen and cold dilute potassium permanganate solution, and it was dehydrogenated by lead tetra-acetate, but not by heating with palladium-black, to give the lactone of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid (XVI), m. p. 255°, which on oxidation with sodium hypobromite was converted into the dicarboxylic acid (IV).

OH ... MeO / MeO — CH$_2$ / CO — O ... Br ... OMe ... OMe   (XIII.)

MeO / MeO — CO / CH·CHO / CH·CO$_2$Et ... CH ... OMe   (XIV.)

CH·OH ... MeO / MeO — CH·CH$_2$OH / CH·CO$_2$H ... CH ... OMe   (XV.)
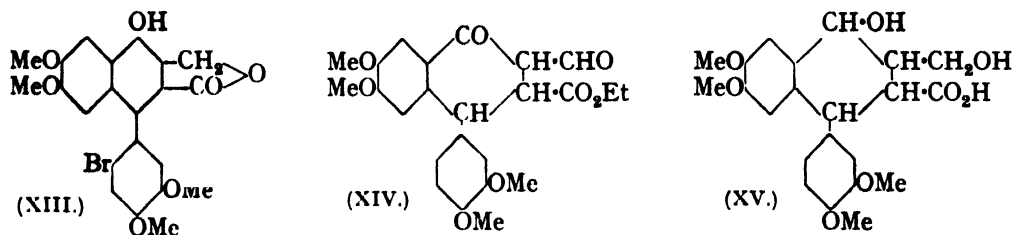
A reaction similar to that observed during the conversion of (XV) into (I ; R = Me) was encountered in another series of experiments. The ethyl ester of the keto-acid (XI) reacted almost quantitatively with ethyl oxalate in the presence of potassium ethoxide, giving a yellow product, probably (XVII). This was reduced with aluminium amalgam in moist ethereal solution to a colourless compound, which was hydrolysed and converted into a lactonic acid, provisionally formulated as the *lactone of 4-hydroxy-6 : 7-dimethoxy-2-carboxy-1-(3′:4′-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene-3-glycollic acid* (XVIII).* This substance crystallises with one molecule of water of crystallisation which cannot be removed without profound decomposition, but the lactonic nature of the compound was established by titration with alkali. When the lactone was heated at 200°, a 25% yield of the β-form of the *lactone of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid* (I ; R = Me), m. p. 208°, was obtained. The formation of this reduced decarboxylation product is obviously analogous to the conversion of (XV) into (I ; R = Me) and is equally difficult to understand. A

* Two alternative formulæ can be derived by including the nuclear CH·OH group in the γ-lactone ring.

further study of (XV), (XVIII), and related compounds is contemplated. The lactone, m. p. 208°, was unaffected by hydrogen in the presence of palladium, but it was de-

MeO—/ —CH₂ >O
MeO— —CO

(XVI.)   OMe
         OMe

MeO— CO— CH·CO·CO₂Et
MeO—   CH·CO₂Et
      CH—

(XVII.)   OMe
          OMe

CH·OH CO₂H
MeO—   CH—CH— >O
MeO—   CH—CO
   CH—

(XVIII.)   OMe
           OMe
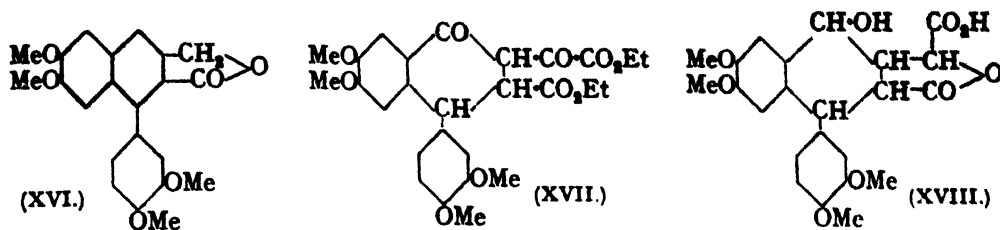
hydrogenated more readily than the α-form described above. Either heating with palladium-black at 250° or treatment with lead tetra-acetate at 70° converted it into the lactone (XVI), m. p. 255°, identical with the substance obtained from the α-form of the lactone (I; R = Me).

It has now been found that " sulphite-liquors lactone " dimethyl ether can be converted into a dehydrolactone, $C_{22}H_{20}O_6$, m. p. 215—216°,* either by heating with selenium or by means of lead tetra-acetate. The dehydrolactone was unattacked by hydrogen in the presence of palladium. Although it differed from the lactone (XVI), m. p. 255°, on oxidation with potassium permanganate, it was converted into the dicarboxylic acid (IV). It must be concluded from these observations that the dehydrolactone, m. p. 215—216°, is the lactone of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic acid (XIX) and that " sulphite-liquors lactone " dimethyl ether must have the structure (II; R = Me). A synthesis of (XIX) is in progress, but the above conclusions are substantiated by the conversion of matairesinol dimethyl ether into a mixture of the lactones (XVI) and (XIX) (see previous communication).

MeO— —CO >O
MeO— —CH₂

(XIX.)

OMe
OMe

MeO— CO₂H
EtO— CO— —OMe
              OEt

(XX.)
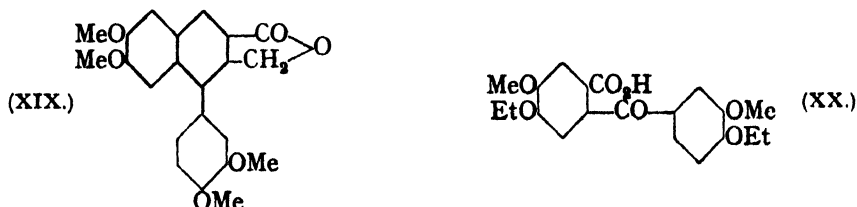
The positions of the phenolic hydroxyl groups in " sulphite-liquors lactone " have been established by preparing the diethyl ether and oxidising this with permanganate to 5-methoxy-4-ethoxy-2-(3′-methoxy-4′-ethoxybenzoyl)benzoic acid (XX), identical with the acid prepared by Vanzetti and Dreyfuss (*loc. cit.*) from *iso*livil. Consequently " sulphite-liquors lactone " must be represented by formula (II; R = H).

The formation of a dibromo-substitution product from " sulphite-liquors lactone " dimethyl ether (Erdtman, *loc. cit.*) may be used as an argument against formula (II; R = Me) and in favour of (III; R = Me). However, it has now been shown that phenyl-naphthalene derivatives, such as the acid (VII) and 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxy-phenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene-3-carboxylic acid, readily yield dibromo-substitution products by the action of bromine in cold acetic acid solution. Although the positions of the bromine atoms have not been established, the formation of a dibromo-derivative can no longer be regarded as an objection to formula (II; R = Me) for " sulphite-liquors lactone " dimethyl ether. Formula (III) can be excluded; it is shown in the previous communication that this formula is required to account for the properties of matairesinol dimethyl ether.

* Dr. Erdtman (private communication) informs us that he had previously prepared this dehydro-lactone by the tetra-acetate method. The amount obtained was insufficient to enable him to crystallise the product to constant m. p., and no analyses were made.

EXPERIMENTAL.

6 : 7-*Dimethoxy*-1-(3' : 4'-*dimethoxyphenyl*)*naphthalene*-2 : 3-*dicarboxylic Acid* (IV).—(With C. R. Mavin) 3 : 4-Dimethoxyphenylpropiolic acid (3·2 g.) (Perkin and Schiess, J., 1904, **85,** 164) was dissolved in boiling acetic anhydride (20 c.c.), and the solution heated at 100° for 4 hours. After cooling, the solid was collected; it crystallised from nitrobenzene (carbon) in pale yellow prisms (2·4 g.), m. p. 305—306° (Found : C, 66·8; H, 4·7. $C_{22}H_{18}O_7$ requires C, 67·0; H, 4·6%). This *anhydride*, which was sparingly soluble in the usual organic solvents, dissolved slowly in boiling 10% sodium hydroxide solution; acidification of the cold alkaline solution precipitated the dibasic *acid* (IV), which crystallised from methyl alcohol–chloroform in slender colourless needles, m. p. 232—234° (Found : C, 64·2; H, 5·0. $C_{22}H_{20}O_8$ requires C, 64·1; H, 4·9%). When the acid is heated above its m. p., it is rapidly converted into the yellow anhydride. The *dimethyl* ester, obtained by boiling the anhydride with methyl-alcoholic hydrogen chloride, crystallised from methyl alcohol in colourless prisms, m. p. 166° (Found : C, 65·4; H, 5·6. $C_{24}H_{24}O_8$ requires C, 65·5; H, 5·5%). The *diethyl* ester crystallised from methyl alcohol in colourless prisms, m. p. 127—128° (Found : C, 66·9; H, 5·9. $C_{26}H_{28}O_8$ requires C, 66·7; H, 6·0%).

β-3 : 4-*Dimethoxybenzoyl*-α-(3' : 4'-*dimethoxybenzylidene*)*propionic Acid* (VI).—Sodium β-(3 : 4-dimethoxybenzoyl)propionate (35 g.), veratraldehyde (40 g.), and acetic anhydride (80 c.c.) were heated at 100° for 12 hours. Water was added and after 4 hours the solid was collected and washed with sodium carbonate solution and then with methyl alcohol. Crystallisation from alcohol containing a little chloroform yielded the *lactone* of (VI) as greenish-yellow plates (34 g.), which melt at 140—147°, resolidify, and melt again at 153°. The lactone can also be crystallised from benzene or acetic acid and the same behaviour was observed on heating (Found : C, 68·5; H, 5·6. $C_{21}H_{20}O_6$ requires C, 68·5; H, 5·4%). The lactone (1·8 g.) was shaken with a solution of sodium (0·12 g.) in methyl alcohol (15 c.c.). When solution was complete, water was added, the alcohol removed, the filtered solution acidified, and the precipitate collected. Crystallisation from either methyl alcohol or benzene yielded the *acid* (VI) in colourless needles (1·5 g.), m. p. 175° (Found : C, 65·4; H, 5·8. $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%).

6 : 7-*Dimethoxy*-1-(3' : 4'-*dimethoxyphenyl*)*naphthalene*-3-*carboxylic Acid* (VII).—(a) The acid (VI) (20 g.) was refluxed for 4 hours with methyl alcohol (100 c.c.) saturated with hydrogen chloride. On cooling, the *methyl* ester of (VII) (17 g.) separated; it yielded the *acid* (VII) (15 g.) on hydrolysis with alcoholic potassium hydroxide. (b) The lactone of acid (VI) (3·6 g.) was kept for 3 days with iodine (3 g.) in chloroform (30 c.c.). Shaking with sodium thiosulphate solution decomposed the greenish-brown solid which had separated, and subsequent removal of the chloroform yielded the acid (VII) (1·5 g.). The acid (VII) crystallised from methyl alcohol containing a little chloroform in colourless slender needles, m. p. 222—223° (Found : C, 68·7; H, 5·4. $C_{21}H_{20}O_6$ requires C, 68·5; H, 5·4%). The methyl ester, obtained as described above or by esterification of the acid, crystallised from methyl alcohol in colourless needles, m. p. 177—178° (Found : C, 68·9; H, 6·0. $C_{22}H_{22}O_6$ requires C, 69·1; H, 5·8%). Acetic acid solutions of the acid (VII) were kept over-night (i) with 1 mol. and (ii) with 4 mols. of bromine. The product from (i) crystallised from 50% acetic acid in slender colourless needles, shrinking at about 280—285° and melting at 295—296°, and gave analytical figures in agreement with an impure *monobromo*-derivative (Found : Br, 14·8; equiv., 459. $C_{21}H_{19}O_6Br$ requires Br, 17·9%; equiv., 447). The product from (ii) crystallised from methyl alcohol-chloroform in colourless prisms, m. p. 260°, having the composition of a *dibromo*-derivative of (VII) (Found : C, 47·6; H, 3·5; Br, 30·9; equiv., 524. $C_{21}H_{18}O_6Br_2$ requires C, 47·9; H, 3·4; Br, 30·4%; equiv., 526).

6 : 7-*Dimethoxy*-1-(3' : 4' -*dimethoxyphenyl*)*naphthalene* (V).—The acid (VII) or the anhydride of (IV) (1 g.) was boiled with quinoline (10 c.c.) and copper powder (0·2 g.) for 2 hours. Ether was added and the quinoline and unchanged acids were removed by washing first with dilute hydrochloric acid and then with sodium hydroxide solution. The ethereal solution was dried, and the solvent removed; the residue crystallised from methyl alcohol in colourless plates, m. p. 159—160° (Found : C, 73·8; H, 6·2. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·1%). When the anhydride of (IV) was employed, the yield of (V) was about 2%, but a 50% conversion of the acid (VII) was obtained. The naphthalene derivative (V) (4 g.) was boiled with hydriodic acid (10 c.c., *d* 1·7) and acetic acid (20 c.c.) for 4 hours. The solvents were removed under reduced pressure and the residue was mixed with zinc dust (10 g.) and distilled. The oily distillate was washed with dilute hydrochloric acid and with sodium hydroxide solution and dried in ether, and the solvent removed. The residue was distilled and the fraction (1·0 g.), b. p. 160—170°/

0·1 mm., was identified as 1-phenylnaphthalene by conversion into the 4-bromo- and the 4-nitro-derivative, m. p.'s 69° and 132° respectively, which were identical with the substances prepared by Weiss and Woidich's method (*Monatsh.*, 1925, 46, 453).

γ-*Di-(3 : 4-dimethoxyphenyl)itaconic Acid* (VIII).—A mixture of 3 : 4 : 3′ : 4′-tetramethoxy-benzophenone (4 g.) (Perkin and Weizmann, J., 1906, 89, 1661) and ethyl succinate (2·4 g.) was boiled for 12 hours with a suspension of potassium ethoxide (from 1 g. of potassium) in benzene (40 c.c.). Ether and water were added, the aqueous layer was mixed with 5% sodium hydroxide solution (10 c.c.) and boiled for 1 hour to complete the hydrolysis of the half ester of (VIII). Acidification precipitated the *acid* (VIII), which, collected after 12 hours, crystallised from acetone–benzene in small needles (3·3 g.), m. p. 128—130° with slight previous softening (Found : C, 59·6; H, 5·8; equiv., 207. $C_{21}H_{22}O_8,H_2O$ requires C, 60·0; H, 5·7%; equiv., 210). The acid can be recrystallised from hot water or glacial acetic acid, but it is sparingly soluble in ether, light petroleum, and benzene. The *anhydride*, obtained by heating the acid (VIII) with acetyl chloride (4 parts) for 2 hours, crystallised from benzene in colourless needles, m. p. 147—148° (Found : C, 65·5; H, 5·3. $C_{21}H_{20}O_7$ requires C, 65·6; H, 5·2%).

1-*Keto-5 : 6-dimethoxy-3-(3′ : 4′-dimethoxyphenyl)indene-2-acetic Acid* (IX).—The anhydride of the acid (VIII) (1 g.) was kept for 24 hours with a solution of aluminium chloride (1 g.) in nitrobenzene (20 c.c.). After the addition of dilute hydrochloric acid, the nitrobenzene was removed in steam; the red solid which separated from the residue crystallised from methyl alcohol or benzene in red plates (0·7 g.), m. p. 216—217° (Found : C, 65·8; H, 5·4. $C_{21}H_{20}O_7$ requires C, 65·6; H, 5·2%). This compound was soluble in sodium bicarbonate solution, and gave a semicarbazone, which crystallised from alcohol in pale yellow nodules, m. p. 254° (decomp.).

5 : 6-*Dimethoxy-3-(3′ : 4′-dimethoxyphenyl)hydrindene-2-acetic Acid*.—The ketone (IX) (0·3 g.) in acetic acid (50 c.c.) was reduced with hydrogen in the presence of palladised charcoal (0·2 g. of 0·5%) during 6 hours. The colourless solution was filtered, and evaporated under reduced pressure; the residue crystallised from methyl alcohol in colourless needles (0·2 g.), m. p. 169—170° (Found : C, 67·6; H, 6·4. $C_{21}H_{24}O_6$ requires C, 67·7; H, 6·5%). This *acid* did not decolorise potassium permanganate in sodium carbonate solution and it could not be converted into a semicarbazone.

Bis-(3 : 4-dimethoxyphenyl)methylsuccinic Acid (X).—This could be prepared by catalytic reduction of the itaconic acid (VIII), but an active platinic oxide catalyst was necessary and the following method was adopted for the preparation of large quantities of the acid. A mixture of acetic acid (150 c.c.) and concentrated sulphuric acid (150 c.c.) was added with stirring to a solution of ethyl hydroxymethylenesuccinate (41 g.) and veratrole (57 g.) in acetic acid (100 c.c.), the temperature being maintained below 15°. After 12 hours, water was added, and the product extracted with chloroform. The solvent was removed and, after being heated at 100° under diminished pressure to remove acetic acid, the oily residue was hydrolysed by boiling with 10% methyl-alcoholic potassium hydroxide (250 c.c.) for 2 hours. The methyl alcohol was removed, water (150 c.c.) added, and the boiling continued for another 2 hours. The *acid* (X), liberated by the addition of hydrochloric acid and isolated with chloroform, crystallised from benzene in colourless needles (72 g.), m. p. 177—178°; a further yield (7 g.) was obtained from the benzene liquors (Found : C, 62·5; H, 6·2. $C_{21}H_{24}O_8$ requires C, 62·4; H, 6·0%).

4-*Keto-6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carb-oxylic Acid* (XI).—The acid (X) (30 g.) was refluxed with acetyl chloride (60 c.c.) for 2 hours. The excess of acetyl chloride was removed and the residue, after being heated at 100° under reduced pressure for 1 hour, was dissolved in nitrobenzene (30 c.c.) and added gradually with stirring to an ice-cold solution of aluminium chloride (21 g.) in nitrobenzene (100 c.c.). After 12 hours, dilute hydrochloric acid was added, the nitrobenzene removed in steam, the residue cooled, and the *acid* (XI) collected, dried at 100°, and crystallised from methyl alcohol containing a little chloroform, colourless needles (26 g.), m. p. 200—201°, being obtained (Found : C, 64·9; H, 5·7. $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%). The *semicarbazone* crystallised from acetic acid in slender needles, m. p. 244—245° (decomp.) (Found : N, 9·7. $C_{22}H_{25}O_7N_3$ requires N, 9·5%). The *ethyl* ester, prepared by refluxing the finely powdered acid (XI) with alcoholic hydrogen chloride (10 parts) for 6 hours, crystallised from alcohol in colourless needles, m. p. 130—131° (Found : C, 66·9; H, 6·4. $C_{23}H_{26}O_7$ requires C, 66·7; H, 6·5%).

6 : 7-*Dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic Acid*.—This can be prepared by reducing the acid (XI), but the best results were obtained with the ethyl ester. The ethyl ester (1 g.) was gently boiled for 12 hours with amalgamated zinc (5 g.) and concentrated hydrochloric acid (10 c.c.). After dilution and cooling, the product

was isolated with chloroform; it crystallised from methyl alcohol in tufts of slender needles, m. p. 184—185° (Found : C, 67·8; H, 6·7. $C_{21}H_{24}O_6$ requires C, 67·7; H, 6·5%). The structure of this *acid* was confirmed by heating with selenium (2 parts) at 280° for 12 hours. The product, isolated with chloroform, crystallised from methyl alcohol (carbon) in colourless plates, m. p. 159—160°, identical with 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)naphthalene (V) (p. 640). A *dibromo-acid* was obtained by the action of bromine (4 mols.) on a chloroform solution of the above carboxylic acid; it crystallised from alcohol in clusters of small colourless prisms, m. p. 190—191° (Found : Br, 30·6. $C_{21}H_{22}O_6Br_2$ requires Br, 30·2%).

Ethyl 3-Bromo-4-keto-6 : 7-dimethoxy-1-(6′-bromo-3′ : 4′-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate.—A solution of bromine (1 g.) in chloroform (10 c.c.) was added to the ester (XI) (1 g.) in chloroform (10 c.c.). After 12 hours, the hydrogen bromide was removed in a current of dry air, the chloroform evaporated, and the residue crystallised from methyl alcohol; colourless prisms (1·7 g.), m. p. 146—147°, were obtained (Found : Br, 28·6. $C_{23}H_{24}O_7Br_2$ requires Br, 28·0%).

Ethyl 4-Hydroxy-6 : 7-dimethoxy-1-(6′-bromo-3′ : 4′-dimethoxyphenyl)naphthalene-2-carboxylate (XII).—The above dibromo-ester (2 g.) was heated with diethylaniline (10 c.c.) at 180—190° for 3 hours. The base was removed in steam; the product, isolated with ether, crystallised from aqueous acetic acid in almost colourless plates (1·5 g.), m. p. 193—195° (Found : C, 56·6; H, 4·8; Br, 16·2. $C_{23}H_{23}O_7Br$ requires C, 56·2; H, 4·7; Br, 16·3%). This *compound* was insoluble in sodium bicarbonate solution but soluble in sodium hydroxide and a red azo-dye was precipitated by the addition of diazotised aniline to its alkaline solution. A stream of hydrogen was passed through a boiling alcoholic solution of (XII) in the presence of a palladised charcoal catalyst. The product, probably *ethyl 4-hydroxy-6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)naphthalene-2-carboxylate,* crystallised from methyl alcohol in colourless prisms, m. p. 228° (Found : C, 66·4; H, 5·7. $C_{23}H_{24}O_7$ requires C, 67·0; H, 5·8%), but numerous attempts to repeat this experiment were unsuccessful.

Lactone of 4-Hydroxy-6 : 7-dimethoxy-1-(6′-bromo- 3′ : 4′-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic Acid (XIII).—The bromophenol (XII) (0·5 g.), 40% formalin (1 c.c.), concentrated hydrochloric acid (2 c.c.), and glacial acetic acid (5 c.c.) were heated at 100° for 3 hours. The brown powder which separated crystallised from nitrobenzene in small buff-coloured prisms, m. p. 319—320° (Found : C, 55·3; H, 4·1. $C_{22}H_{19}O_7Br$ requires C, 55·6; H, 4·0%). This *lactone* was insoluble in sodium bicarbonate solution, but no precipitation occurred when solutions of this compound in sodium hydroxide were saturated with carbon dioxide. Diazonium compounds did not couple with the lactone in alkaline solution.

Ethyl 3-Aldehydo-4-keto-6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate (XIV).—The ethyl ester of the tetralonecarboxylic acid (XI) (8 g.), ethyl formate (4 c.c.), and sodium wire (1 g.) were allowed to react in benzene (40 c.c.) for 12 hours. Water was added, the aqueous layer acidified, and the product extracted with ether and dried. Removal of the ether gave a compound, which crystallised from methyl alcohol containing a little chloroform in large prisms (7·3 g.), m. p. 165° (Found : C, 65·0; H, 6·1. $C_{24}H_{26}O_8$ requires C, 65·2; H, 5·9%). This *hydroxymethylene* compound was soluble in sodium hydroxide solution, and addition of ferric chloride to a solution of (XIV) in alcohol produced a deep green coloration. Boiling with alcoholic potassium hydroxide converted the hydroxymethylene compound into the tetralonecarboxylic acid (XI), m. p. 205°.

4-Hydroxy-6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic Acid (XV).—4% Sodium amalgam (50 g.) was gradually added to a solution of the above hydroxymethylene compound (1 g.) in 0·2% sodium hydroxide solution (50 c.c.) at 100°; excessive alkalinity was prevented by a continuous stream of carbon dioxide. When the amalgam was exhausted, the clear solution was acidified; the product, isolated with chloroform, crystallised slowly from a small amount of methyl alcohol in small plates (0·2 g.), m. p. 195—197°, raised to 200° by a further crystallisation (Found : C, 63·4, 63·3; H, 6·5, 6·3; equiv., 420. $C_{22}H_{26}O_8$ requires C, 63·2; H, 6·2%; equiv., 418). The methyl-alcoholic liquors gave 0·2 g. of the lactone when treated with acids as described below.

α-Form of the Lactone of 6 : 7-Dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate (I; R = Me).—This was prepared either (a) by heating the acid (XV) at 200° for 10 minutes or (b) by boiling the acid with 10% sulphuric acid (20 parts) for 2 hours. The product was washed in chloroform with sodium bicarbonate solution, and the chloroform removed. The residue separated from methyl alcohol, containing a little chloroform, in a gelatinous form, which was converted into a crystalline powder (yield, 70%), m. p. 170—175°, by drying at 100°. Repeated crystallisation either from the same solvent or

from 60% formic acid gave colourless nodules (yield, 40%), m. p. 186—187° (Found : C, 68·7, 68·6; H, 6·3, 6·4. $C_{22}H_{24}O_8$ requires C, 68·7; H, 6·3%). Attempts to reduce this *lactone* were unsuccessful. It sublimed when heated to 250°/0·1 mm. and could not be dehydrogenated by heating with palladium-black.

Lactone of 4-Hydroxy-6 : 7-dimethoxy-2-carboxy-1-(3′ : 4′-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydronaphthalene-3-glycollic Acid (XVIII).—A mixture of ethyl oxalate (1·2 c.c.) and the ethyl ester of the tetralonecarboxylic acid (XI) (2 g.) in benzene (7 c.c.) was poured into a suspension of potassium ethoxide (from 0·3 g. of potassium and 0·5 c.c. of alcohol) in ether (30 c.c.). After 2 hours, water (70 c.c.) was added, and the yellow aqueous layer was separated and acidified. The caseous yellow precipitate, which gave a violet colour with ferric chloride, was extracted with ether and the moist ethereal extract (100 c.c.) was poured on aluminium amalgam (from 5 g. of aluminium). After 12 hours, the colourless solution was removed from the hydroxide, which was washed with ether. The combined ethereal extracts were evaporated, and aqueous sodium hydroxide was gradually added to a boiling solution of the residual oil (1·8 g.) in a little methyl alcohol, until permanent alkalinity was obtained. Water was added, the methyl alcohol removed, and the residue acidified and boiled for 10 minutes. The precipitate, after being dried, crystallised from methyl alcohol in colourless needles (0·8 g.), m. p. 212—213° (decomp.) [Found : C, 59·8, 59·5; H, 5·6, 5·6; equiv. (by titration), 456; (by back titration), 231. $C_{22}H_{26}O_{10}$ requires C, 59·7; H, 5·6%; equivs., 462 and 231]. These figures agree with a monohydrate, but we have been unable to prepare the anhydrous form of (XVIII). Several reactions of this lactone are difficult to explain. When refluxed with ethyl-alcoholic hydrogen chloride, it was converted into a *diethyl* ester, which crystallised from benzene–light petroleum in slender needles, m. p. 145—146° (Found : C, 64·8, 65·1; H, 6·5, 6·6. $C_{27}H_{32}O_9$ requires C, 64·8; H, 6·4%). Hydrolysis with methyl-alcoholic potassium hydroxide converted this ester into a *carboxylic acid*, which crystallised from methyl alcohol in colourless prisms, m. p. 212—213° (Found : C, 61·4; H, 5·5. $C_{22}H_{24}O_9$ requires C, 62·1; H, 5·4%), and depressed the m. p. of the hydrated form described above. When the hydrated lactone was heated for 10 minutes at 215°/12 mm., it was converted into an acidic *compound*, which was sparingly soluble in chloroform and methyl alcohol, but crystallised from acetic acid in red-orange plates, m. p. 285° (Found : C, 67·1, 67·1; H, 5·1, 4·9. $C_{22}H_{20}O_7$ requires C, 66·7; H, 5·1%).

β-*Form of the Lactone of 6 : 7-Dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic Acid* (I; R = Me).—The lactonic acid (XVIII) (0·1 g.) was heated in an oil-bath at 215° for 10 minutes; the product hardened on trituration with methyl alcohol and crystallised from methyl alcohol–chloroform in cream-coloured prisms (0·045 g.), m. p. 209—210°. Colourless prisms, m. p. 209—210°, were obtained by sublimation at 0·1 mm. (Found : C, 68·6, 68·4, 68·8; H, 6·3, 6·0, 6·1. $C_{22}H_{24}O_6$ requires C, 68·7; H, 6·3%). This *compound* was insoluble in sodium bicarbonate solution, slowly soluble in boiling aqueous sodium hydroxide, and rapidly dissolved by warm alcoholic alkali, subsequent addition of water producing no precipitate.

Lactone of 6 : 7-Dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic Acid (XVI).—(a) Either the α- or the β-form of the lactone (I; R = Me) (0·2 g.) and lead tetra-acetate (0·4 g.) in acetic acid (10 c.c.) were heated at 70° for 10 minutes. Water was added, the product extracted with chloroform and washed with water and sodium bicarbonate solution, and the solvent removed. The residue rapidly hardened on boiling with methyl alcohol. The conversion of the β-form was almost quantitative, but dehydrogenation of the α-form occurred to an extent of 10% only and a large amount of unchanged material was recovered. (b) The β-form of the lactone (I; R = Me) (0·1 g.) and palladium-black (0·02 g.) were intimately mixed and heated at 220—230° for ¼ hour. The pressure was then reduced to 0·1 mm., and the temperature raised to 255° for ¼ hour. The sublimate (0·07 g.) was collected. The α-form of the lactone (I; R = Me) was recovered after similar treatment. The products from experiments (a) and (b) were identical, and crystallised from methyl alcohol–chloroform in stout colourless prisms, m. p. 254—255° (Found : C, 69·2, 69·4; H, 5·4, 5·3. Calc. for $C_{22}H_{20}O_6$: C, 69·5; H, 5·3%). This lactone dissolved to a pale yellow solution in concentrated sulphuric acid, which gradually became red. Concentrated nitric acid gave a deep brownish-red colour. The lactone was hydrolysed slowly with boiling sodium hydroxide solution, but rapid hydrolysis occurred with alcoholic alkali. The lactone (0·2 g.) was dissolved in 1% methyl-alcoholic sodium hydroxide (10 c.c.) by boiling for 1 hour. Water (10 c.c.) was added, the methyl alcohol removed, and a solution of bromine (0·25 c.c.) in 10% sodium hydroxide solution (6 c.c.) added. After heating at 100° for 3 hours, the solution was filtered, acidified, and extracted with chloroform. The solvent was removed, and the residue heated for 1 hour on the water-bath with

excess of acetyl chloride. The solid which separated crystallised from nitrobenzene in pale yellow prisms, m. p. 304—306°, identical with the anhydride of the dibasic acid (IV).

Lactone of 6 : 7-Dimethoxy-1-(3' : 4'-dimethoxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic Acid (XIX).—α-" Sulphite-liquors lactone " dimethyl ether was not dehydrogenated by heating with palladium-black, but (XIX) was obtained in 70% yield by dehydrogenation with lead tetra-acetate as described above in the preparation of the lactone of (XVI). Also α-" sulphite-liquors lactone " dimethyl ether (0·5 g.) was heated with selenium (0·5 g.) at 255—260° for 1 hour and then at 275° for 6 hours. The product, isolated with chloroform, was crystallised several times from methyl alcohol, yielding (XIX) (0·1 g.). The lactone (XIX) crystallised from methyl alcohol, containing a little chloroform, in slender prisms, m. p. 215—216° (Found : 69·4; H, 5·4. Calc. for $C_{22}H_{20}O_6$: C, 69·5; H, 5·3%). This lactone dissolved in concentrated sulphuric acid to a cherry-red solution, which became brown on addition of a drop of concentrated nitric acid. The behaviour of this lactone to alkalis was similar to that of the isomeric lactone of (XVI), but it could not be oxidised with sodium hypobromite.[*]

An alkaline solution of the lactone (XIX) (0·25 g.) was prepared as described above in the case of the isomeric lactone (XVI). The cold solution was saturated with carbon dioxide, and finely powdered potassium permanganate (0·3 g.) added during 3 hours. The liquid was filtered and acidified, and the product, isolated with chloroform, was converted into the anhydride of the dibasic acid (IV), m. p. 305—306°.

" *Sulphite-liquors lactone* " *Diethyl Ether.*—Ethyl sulphate (2 c.c.) was added to a solution of " sulphite-liquors lactone " (1 g.) in 2·7% aqueous sodium hydroxide (30 c.c.). After being stirred for 1 hour at 100°, the solution was cooled to 15°, 1% aqueous sodium hydroxide (30 c.c.) added, and the stirring continued for another hour at 15°. The solution was acidified and heated at 100° for 3 hours. The product crystallised from alcohol in slender felted needles (1·1 g.), m. p. 178—179° (Found : C, 69·7; H, 7·0. $C_{24}H_{28}O_6$ requires C, 69·9; H, 7·0%). This *diethyl ether* (2 g.) was oxidised with potassium permanganate as described by Erdtman (*loc. cit.*) in the case of the corresponding dimethyl ether. 5-Methoxy-4-ethoxy-2-(3'-methoxy-4'-ethoxybenzoyl)benzoic acid (0·08 g.), m. p. 213—214°, was obtained, and converted into the corresponding anthraquinone, m. p. 288° (Vanzetti and Dreyfuss give 214° and 288° respectively).

Our thanks are due to Professor B. Holmberg and Dr. H. Erdtman for the " sulphite-liquors lactone " used in this research.

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143. *Syntheses of Polycyclic Compounds Related to the Sterols. Part IV. The Identification of 3'-Methyl-1 : 2-cyclopentenophenanthrene and its Preparation from Cholesterol.*

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IN Part II it was concluded, from a comparison of the hydrocarbon $C_{18}H_{16}$ (D) resulting from the dehydrogenation of sterols and bile acids (Diels, Gädke, and Körding, *Annalen*, 1927, **459**, 1) with 3'-methyl-1 : 2-*cyclo*pentenophenanthrene (K) prepared synthetically (Harper, Kon, and F. Ruzicka, *J.*, 1934, 124), that these hydrocarbons are identical; this conclusion received strong support from the crystallographic examination of these compounds and of their derivatives by Bernal and Crowfoot (this vol., p. 93). Since then, Hillemann (*Ber.*, 1935, **68**, 102) has prepared from the hydrocarbon (B) synthesised by Bergmann and himself (*ibid.*, 1933, **66**, 1302) the nitroso-derivative already obtained by Diels *et al.* (*loc. cit.*) from D, whilst Diels and Rickert (*Ber.*, 1935, **68**, 267) have prepared the same tribromo-derivative from both D and K, thus further confirming their identity; and we have since obtained this compound from B.

It nevertheless appeared desirable to elucidate the nature of the small differences

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[*] Erdtman (*loc. cit.*) converted " sulphite-liquors lactone " dimethyl ether into the corresponding dibasic acid by the action of sodium hypobromite, and the difficulty now experienced is probably due to a steric effect introduced by the planar configuration of the lactone (XIX).

observed between the hydrocarbons of different origin, and also between their derivatives, bearing in mind their importance for the diagnosis of a sterol-like skeleton in many natural products.

When the hydrocarbon K was prepared with care to avoid overheating in the course of dehydrogenation, the product only differed from B in that its solutions had a strong blue fluorescence in daylight, and the picrate, although identical in appearance, melted at 127—128°; the other derivatives had identical properties :

	Hydrocarbon.	Trinitrobenzene compound.	Trinitrotoluene compound.	Styphnate.
M. p.	125—126°	148—149°	96—97°	135—136°

The hydrocarbon was then further purified by chromatographic adsorption, already successfully employed by Diels and Rickert (*loc. cit.*); the product no longer gave fluorescent solutions and in ultra-violet light the fluorescence was violet, not blue. The m. p. of the picrate was now 130—131°, or about 1° lower than that of the purest B, and was not altered by recrystallisation.

A hydrocarbon of identical properties has also been isolated by repeated purification, by the adsorption method, of a sample of D prepared from cholesterol; we wish to emphasise that this material also showed no fluorescence in daylight and exhibited a property commented on by Diels and Rickert (*loc. cit.*) as being characteristic of K, namely, that the crystals separating from an alcoholic solution lose their lustre when the solution attains room temperature.

The purest specimen of D gave a picrate, m. p. 127—128°, unaltered by repeated crystallisation, and the other derivatives had the properties already recorded for the corresponding derivatives of B and K.

It can therefore be concluded that substantially pure 3'-methyl*cyclo*pentenophenanthrene has been isolated from the dehydrogenation product of cholesterol. The varying melting points of the picrate are not due to a gross impurity, no trace of which could be revealed by analysis, but are probably attributable to the formation of variable quantities of the second form of the picrate, namely, the stable form, m. p. 117°, of Bernal and Crowfoot (*loc. cit.*).* It follows that the picrate has little diagnostic value for the identification of the hydrocarbon, but both the styphnate (Gamble and Kon, this vol., p. 443) and the *s*-trinitrobenzene compound are suitable; the trinitrotoluene compound is somewhat soluble and therefore not to be recommended for small-scale work. The purification of the tribromo-derivative also requires a fairly large amount of material, and the nitroso-derivative is altogether unsuitable.

<center>EXPERIMENTAL.</center>

Hydrocarbon K.—The preparation was carried out essentially as described by Harper, Kon, and Ruzicka (*loc. cit.*), but the use of naphthylethyl bromide in place of the chloride is advantageous. The nature of the magnesium is also important, the best result being obtained with a sample supplied by the Mallinckrodt Chemical Co. of Philadelphia; it is advisable to use a 50% excess of magnesium and to add the ketone very soon after all the bromide has been introduced.

In the dehydrogenation of the hydrocarbon $C_{19}H_{30}$ it is important not to exceed a bath temperature of 330°; the formation of the high-melting by-product is almost entirely prevented in this way. The hydrocarbon was distilled and converted into the picrate, m. p. 127—128° (constant) after two crystallisations from benzene–alcohol (1 : 5). The hydrocarbon was regenerated from the picrate and repeatedly crystallised from alcohol. A portion was reconverted into the picrate, and this repeatedly crystallised from alcohol–benzene, a product of m. p. 129—130° being obtained; the other derivatives prepared had the correct m. p.'s given above.

Finally, the hydrocarbon was subjected to chromatographic adsorption, following the method of Winterstein and Stein (*Z. physiol. Chem.*, 1933, **220**, 247) and Diels and Rickert (*loc. cit.*);

* [Added in proof.] The authors are indebted to Miss D. Crowfoot for a crystallographic examination of the three hydrocarbons and their picrates. The hydrocarbons were indistinguishable, but the picrate of D differed from those of B and K in the much slower conversion of the metastable into the stable form, a result in agreement with the view expressed above.

it is advantageous to use rather more solvent than is recommended by the latter authors. 1·5 G. of the hydrocarbon in 150 c.c. of petroleum (b. p. 70—80°) were allowed to percolate through a column of about 100 g. of alumina contained in a tube 22 mm. wide; 300 c.c. of the same solvent were then used for " developing." After two treatments the hydrocarbon was recovered, recrystallised from alcohol, and used for the preparation of derivatives; the picrate, which formed fine orange-yellow needles, had m. p. 130—131°.

Hydrocarbon B.—The specimen was prepared as described by Bergmann and Hillemann (*loc. cit.*); it could not be satisfactorily purified by crystallisation and was therefore converted into the picrate; this was recrystallised, and the hydrocarbon regenerated from the pure compound, m. p. 131—132°. The specimen was then distilled under 0·2 mm. pressure, as recommended by Hillemann (*loc. cit.*), a colourless distillate being obtained. The compound, recrystallised from alcohol, formed plates, m. p. 125—126°; the needle-shaped form previously observed (Harper, Kon, and Ruzicka, *loc. cit.*) was not obtained. The hydrocarbon, though pure, has less tendency to form well-defined crystals than K. The picrate prepared from the pure hydrocarbon was exactly like that of K in appearance and had m. p. 131—132°.

Hydrocarbon D.—250 G. of dry cholesterol were dehydrogenated with 500 g. of selenium by heating for 3 hours at 280° and for 50 hours at 330—360° (Ruzicka, Goldberg, and Thomann, *Helv. Chim. Acta,* 1933, **16,** 812); 160 g. of oil were recovered and fractionated at 0·8—0·4 mm. : (1) below 115°, 2·0 g.; (2) 115—158°, 4·8 g.; (3) 158—190°, 45·0 g., solidified in part; (4) 190—213°, 37·5 g., solidified in part; (5) 213—245°, 47·2 g. of light brown oil; (6) 245—295°, 20·7 g. of dark brown gum. The last four fractions were refractionated, fractions being collected at 10° intervals. Four fractions collected below 190°, together with fraction (2) above, were each dissolved in benzene and treated with an equal weight of *s*-trinitrobenzene in hot alcohol-benzene. The trinitrobenzene compound formed was dissolved in cold *cyclo*hexane (which left behind the excess of trinitrobenzene), recovered by evaporation under reduced pressure, and fractionally crystallised from alcohol-benzene. Orange-yellow needles, m. p. 146—147°, were obtained after 10—15 crystallisations.

A further quantity of this material was derived from the fractions of b. p. 190—200° and 200—210°, which were redistilled over sodium, yielding a colourless oil. This solidified to a large extent; the solid was rubbed with cold pentane, filtered off, and treated with trinitrobenzene as above. The higher fractions of the oil did not react with trinitrobenzene.

The hydrocarbon recovered from the trinitrobenzene compound by means of stannous chloride was recrystallised from alcohol (charcoal) and formed indefinite, somewhat coloured plates, m. p. 126—129°; a pure individual compound could not be obtained from it by the usual methods.

The crude hydrocarbon (1·5 g.) was then treated with alumina as described above; a colourless, well-crystallised material was recovered after two treatments, but this still melted somewhat high and therefore the process was repeated twice more; 1·0 g. of hydrocarbon was obtained, m. p. 124—125° with previous sintering, 125—126° after three crystallisations from alcohol (Found : C, 92·8, 93·0; H, 6·9, 6·8. Calc. : C, 93·1; H, 6·9%). The picrate prepared from this was in every way similar to the picrate of K, but melted at 127—128° (Found : C, 62·5; H, 4·1. Calc. : C, 62·5; H, 4·1%); the other derivatives had the correct m. p.'s given on p. 645.

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144. *Some Reactions of* o-*Hydroxybenzylacetone.*

By Wilson Baker and James Walker.

The reduction of *o*-hydroxybenzylideneacetone with sodium amalgam (Harries, *Ber.,* 1891, **24,** 3180; Harries and Busse, *Ber.,* 1895, **28,** 501) gives *o*-hydroxybenzylacetone (I). The same substance has also been prepared by catalytic reduction in presence of platinum-black (50% yield) (Nomura and Nozawa, *Sci. Rep. Tohuku Imp. Univ.,* 1918, **7,** 85), and in presence of a palladised strontium carbonate catalyst (80% yield) (this paper).

Catalytic reduction of *o*-hydroxybenzylideneacetone in methyl- or ethyl-alcoholic solution in presence of palladium chloride gave a mixture of (I) and (II; R = Me or Et),

separated by dissolving the former in aqueous sodium hydroxide. This ready formation of six-membered cyclic acetals is closely analogous to the production of the methylglycosides
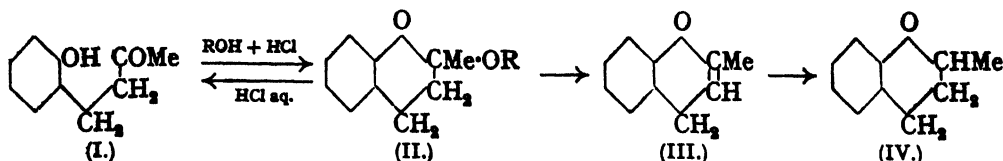
of the sugars, and is probably the first example of its kind in the aromatic series. In the purely aliphatic series Bergmann and Miekeley (*Ber.*, 1922, **55**, 1390) have shown that δ-acetyl-*n*-butyl alcohol gives a cyclic acetal with methyl alcohol and hydrogen chloride at room temperature. The formation of (II) is to be attributed to the presence of hydrogen chloride arising from the reduction of the palladium chloride; this is evident from the results obtained with the metallic platinum catalyst (Nomura and Nozawa, *loc. cit.*) and with the palladised strontium carbonate catalyst. 2-*Ethoxy-2-methylchroman* (II; R = Et) is readily prepared from (I) by the action of hydrogen chloride in ethyl alcohol, and is easily reconverted into (I) by heating with dilute hydrochloric acid; it is completely stable towards hot alkaline solutions.

o-Hydroxybenzylacetone (I), kept in ethereal solution over anhydrous sodium sulphate for two weeks, was converted into 2-*methylchromene* (III), probably through the intermediate (II; R = H). (III) was also obtained by boiling (II; R = Et) with acetic anhydride. Catalytic reduction of (III) gave 2-*methylchroman* (IV) as the sole product; reduction of the aromatic nucleus could not be effected.

2-Methylchroman is described in the literature, but it is very doubtful if it has previously been obtained in anything approaching a state of purity. Harries and Busse (*loc. cit.*) treated (I) in alcoholic solution with zinc dust and hydrochloric acid, and obtained a liquid, b. p. 223—226°/762 mm., with a coumarin-like odour, the analyses of which did not agree well with the formula (IV) and indicated an appreciable alteration during distillation. Compounds (II; R = Me and Et) actually have odours recalling that of peppermint, whereas both (III) and (IV) have an unpleasant "hydrocarbon" odour resembling that of naphthalene. We are of the opinion that Harries and Busse's product was a mixture containing a large amount of (II; R = Et) accompanied by (III) and (IV), a view which is confirmed by a comparison of the relevant boiling points. The product, b. p. 223°, prepared by Stoermer and Schäffer (*Ber.*, 1903, **36**, 2863) had an odour of peppermint and coumarin; it also is probably not 2-methylchroman. Borsche and Geyer (*Ber.*, 1914, **47**, 1154) have described the preparation of "2-methylchromane" from (I) and zinc chloride, but the compound, b. p. 225°, was not examined or analysed.

EXPERIMENTAL.

o-Hydroxybenzylacetone (I).—*o*-Hydroxybenzylideneacetone (30 g.) (Harries, *loc. cit.*) in methyl alcohol (180 c.c.) and a 2% palladised strontium carbonate catalyst (12 g.) were shaken in hydrogen at 3 atmospheres until the required absorption had taken place, the time varying with different specimens of catalyst. The reaction mixture was filtered and fractionated; *o*-hydroxybenzylacetone (24 g.; 80% yield) distilled as a colourless viscous oil at 167—170°/16 mm. (Nomura and Nozawa, *loc. cit.*, give b. p. 160—167°/14·5 mm.). No product distilled below 145°/16 mm. Towards the end of the distillation the oil on the walls of the Claisen flask developed a violet colour (see below).

2-*Ethoxy-2-methylchroman* (II; R = Et).—(A) *o*-Hydroxybenzylideneacetone (16 g.) in ethyl alcohol (75 c.c.) was reduced by hydrogen in presence of palladium chloride (0·5 g.), the absorption being complete in 5 hours. The solution was filtered, diluted with aqueous sodium hydroxide, and extracted with ether and the extracts were shaken with dilute aqueous sodium hydroxide, dried over sodium sulphate, and distilled, leaving an almost colourless, mobile liquid (10 g.; 53% yield), b. p. 105°/11 mm. (Found : C, 74·6; H, 8·2. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). The *chroman* has a rather faint odour of peppermint, and tends to acquire a pink tint on keeping; $n_D^{14·5}$ 1·513. When distilled under ordinary pressure, b. p. 225°/760 mm., it acquires the odour of the chromene (III), and the rise of the refractive index also indicates

a partial conversion into this compound. The alkaline solutions (above) were acidified, and yielded to ether o-hydroxybenzylacetone (I) (6·2 g.; 40% yield). (B) o-Hydroxybenzylacetone (7 g.) in ethyl alcohol (30 c.c.) containing a trace of hydrogen chloride was kept at room temperature for 16 hours, refluxed for 2 hours, and added to a large excess of sodium hydroxide solution (5%). The oil was extracted with ether, dried, and distilled, b. p. 110—111°/17 mm. (6·2 g.), $n_D^{16°}$ 1·512.

2-Methoxy-2-methylchroman (II; R = Me).—o-Hydroxybenzylideneacetone· (10 g.) was reduced in methyl alcohol under the conditions described above. There were isolated o-hydroxybenzylacetone (3·9 g.) and an alkali-insoluble liquid (5·3 g.), b. p. 107°/14 mm. (Found : C, 74·7; H, 8·1. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·8%). The first few drops of the distillate had the odour of the chromene (III); this fact, and the analytical figures, indicated that the substance is probably not completely stable towards distillation. It had an odour very similar to that of the ethoxy-derivative, but rather more sharp; $n_D^{14°}$ 1·523.

2-Methylchromene (III).—(A) A specimen of o-hydroxybenzylacetone was preserved for 2 weeks in ethereal solution over anhydrous sodium sulphate. The product distilled at 95—97°/10 mm. as a colourless mobile oil with an odour recalling that of naphthalene; $n_D^{12°}$ 1·551 (Found : C, 82·3; H, 6·9. $C_{10}H_{10}O$ requires C, 82·2; H, 6·8%). When it was treated with an oxidising agent (chloranil) in presence of concentrated hydrochloric acid, an intense purple colour was developed [see preparation of (I), above]. (B) Compound (II; R = Et) was boiled with twice its weight of acetic anhydride for 2 hours, and then heated with water. An ethereal extract was shaken with sodium bicarbonate solution, dried, and distilled, yielding a colourless liquid, b. p. 95°/11 mm., having all the properties of that prepared under (A).

2-Methylchroman (IV).—2-Methylchromene (1·2 g.) in pure glacial acetic acid (12 c.c.) was shaken in hydrogen under slightly more than atmospheric pressure with a platinum–silica gel catalyst (0·5 g.; No. 17 of the Membranfilter Gesellschaft). Absorption of 1 mol. of hydrogen was complete in 4 hours, and no further absorption took place. The liquid was filtered, poured into water, and extracted with ether. The ethereal solution was washed thoroughly with sodium carbonate solution, dried, and fractionated under diminished pressure. 2-*Methylchroman* (0·9 g.) was obtained, b. p. 100—102°/11 mm., as a colourless mobile oil with an odour resembling that of the unsaturated compound; $n_D^{13·5°}$ 1·532 (Found : C, 80·9; H, 8·2. $C_{10}H_{12}O_2$ requires C, 81·1; H, 8·1%).

An attempt to reduce 2-methylchromene to the fully saturated octahydro-compound, 2-methylhexahydrochroman, with Adams's platinum oxide catalyst proceeded only to the chroman stage.

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145. *Addition Compounds of the Carbohydrates.   Part II.*
Potassium Hydroxide–Sucrose.

By Edmund G. V. Percival.

Sucrose forms a large number of compounds with metallic oxides and hydroxides, the compounds with strontium hydroxide indeed forming a basis of sugar refining. From a survey of the literature, it seems clear that, although various molecular proportions of metallic hydroxides may be associated with one molecule of sucrose, no trustworthy evidence exists pointing to the occurrence of compounds containing more than three molecules of the inorganic components as in $C_{12}H_{22}O_{11},3CaO,3H_2O$ (v. Lippmann, 1904, " Chemie der Zuckerarten," 3 Aufl., 1338; Mackenzie and Quin, J., 1929, 951).

Physicochemical methods such as the phase-rule studies of Reinders and Klinkenberg (*Rec. trav. chim.*, 1929, **48**, 1227), the examination of the decline in specific rotation of sucrose solutions in the presence of alkali (Thomsen, *Ber.*, 1881, **14**, 1647), or the conducto-metric analyses of Hirsch and Schlags (*Z. physikal. Chem.*, 1929, *A*, **141**, 387) are valuable in indicating that compound formation between sucrose and alkalis does occur. The last authors point out that in aqueous solution sucrose behaves as a weak dibasic acid,

$K_1 = 3.1 \times 10^{-13}$, $K_2 = 3.0 \times 10^{-14}$ at 25°. It is significant that the second stage of ionisation is about twice as great as for glucose, which may account for the fact that the sucrose derivatives are more complex.

In Part I of this series (J., 1934, 1160) it was concluded that the probable formulation of compounds of this type was similar to that of the stable monohydrates of the alkali-metal hydroxides and involved co-ordination between the hydroxyl ion of the hydroxide and the most active hydrogen atoms of the sugar concerned, notably in the case of glucose the mobile hydrogen atom in the reducing group associated with the pyranoid ring formation.

The results of the present investigation are in harmony with these conclusions, although, in the absence of a reducing group, the primary alcoholic residues in sucrose appear to be the centres of acidity and each of the three appears to be associated with the potassium hydroxide in the compound $C_{12}H_{22}O_{11},3KOH$ studied. The basis of this conclusion rests on the isolation, on treatment with methyl sulphate under mild conditions, of a trimethyl sucrose in which the primary alcohol residues alone are substituted.
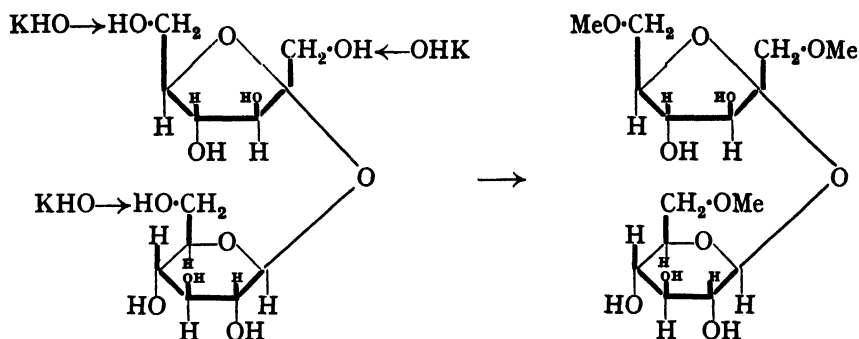
Addition compounds of sucrose and potassium hydroxide were prepared by the action of concentrated alcoholic potassium hydroxide both on sucrose octa-acetate and on an aqueous-alcoholic solution of the free sugar. By the indirect method of analysis (see Part I) it was established that three potassium hydroxide residues were the maximum number which one sucrose molecule would hold in combination, although in ordinary preparations, after washing with alcohol and ether, direct analysis revealed compositions ranging from $C_{12}H_{22}O_{11},KOH$ to $C_{12}H_{22}O_{11},3KOH$, which explains the isolation by Pfeiffer and Tollens (*Annalen*, 1881, **210**, 296) of a monopotassium derivative after continued washing with alcohol. Whether the tripotassium compound is decomposed completely into the free sugar and potassium hydroxide in contact with alcohol or whether in contact with more dilute alkaline solutions only mono- and di-potassium hydroxide derivatives can exist is not clear, although the latter conclusion would seem more probable.

Products approximating in composition to $C_{12}H_{22}O_{11},3KOH$ were treated with methyl sulphate for a brief period and after removal of unchanged sucrose (90%), followed by acetylation, a glass was obtained which on analysis was shown to be a trimethyl penta-acetyl sucrose. Hydrolysis produced no optical inversion, so it was clear that the resulting methylated fructose was of the furanose type as in the case of the hydrolysis of octamethyl sucrose by Haworth and Law (J., 1916, **109**, 1314). By the formation of the furanosides, followed by acetylation and distillation in a high vacuum, it was found possible to separate these hydrolysis products into a methyl tetra-acetyl methylgluco-furanoside and a dimethyl triacetyl methylfructofuranoside.

The former after hydrolysis was recognised as a genuine derivative of glucopyranose, since methylation yielded 2 : 3 : 4 : 6-tetramethyl methylglucoside giving on hydrolysis crystalline 2 : 3 : 4 : 6-tetramethyl glucopyranose, and that the methyl group occupied the primary alcohol residue was proved by the isolation of crystalline 6-methyl glucose phenylosazone.

On account of the positive specific rotation of the dimethyl fructose (II) obtained on

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hydrolysis of the fructofuranoside (I) it was suspected that a derivative of fructofuranose was concerned. This would imply the presence of one methoxyl group in the 6-position to prevent reversion to the more stable pyranose form. Complete methylation of (II) to a tetramethyl methylglycoside (III), followed by oxidation with nitric acid (Avery, Haworth, and Hirst, J., 1927, 2313), gave rise to a tetramethyl lactol acid which on appropriate treatment yielded crystalline 2 : 3 : 4 : 6-tetramethyl fructofuronamide (IV) identical with that obtained from tetramethyl fructofuranose, thus establishing the furanose ring and the participation of the primary alcohol residue at the 6-position in the original methylation.

MeO·CH₂ ... OH ... CH₂·OMe ... OH H (II.) → MeO·CH₂ ... OMe ... CH₂·OMe ... OMe H (III.) → MeO·CH₂ ... OMe ... CO·NH₂ ... OMe H (IV.)

↑

MeO·CH₂ ... OMe ... CH₂·OMe ... OAc H (I.) → MeO·CH₂ ... OH ... CO₂H ... OH H (V.) → MeO·CH₂ ... CO ... OH H (VI.)
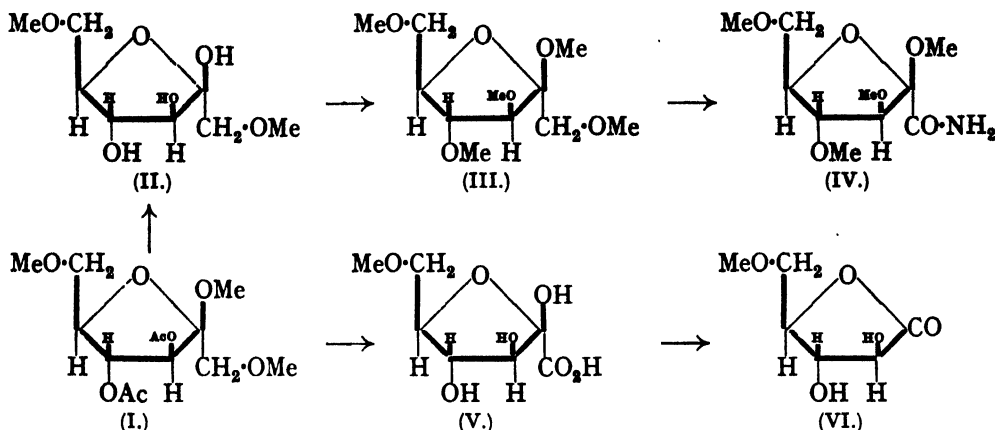
It remained to indicate the position of the second methoxyl residue. Because the free dimethyl sugar failed to form an osazone, substitution in the 1-position was indicated, and this was confirmed as follows. By direct oxidation of the diacetyl dimethyl fructofuranoside under similar conditions to those employed for the tetramethyl derivative, a lactol acid was obtained (V) containing only one methoxyl residue. This was converted into the monomethyl arabonolactone (VI) by treatment with the calculated quantity of acid permanganate (Haworth and Learner, J., 1928, 619), and this lactone was found to have the properties of a γ-lactone, confirming the view that the terminal position is occupied. The position of the second methoxyl group in the dimethyl fructofuranose (II) on the secondary alcohol residues is obviously excluded, since only a monomethyl γ-arabono-lactone resulted on oxidation (VI), the methyl group at the first carbon atom having disappeared on oxidation at that point.

Evidence is thus provided that the trimethyl sucrose obtained by direct methylation of $C_{12}H_{22}O_{11}$,3KOH is substituted only at the three primary alcohol groups present in the molecule. If, therefore, it is considered, as in Part I (*loc. cit.*), that the methyl groups have entered at the points of maximum acidity in the sucrose molecule, it is probable that these primary alcohol residues are involved in the addition compounds of sucrose with alkaline hydroxides. Since the association of sugar and alkali is an unstable one as indicated by the large amount of unconverted sucrose which is recovered from the methylation, there is no evidence that the compounds considered are substitution products, although Pfeiffer and Tollens (*loc. cit.*) described a monosodium derivative which was prepared in a similar manner to $C_{12}H_{21}O_{11}Na$ on the basis of a direct analysis. Their results are, however, just as readily interpreted on the theory of the formation of an addition compound.

Lest it should be considered that the methylation of addition compounds of the type under discussion is due merely to the presence of a certain amount of free potassium hydroxide which, reacting with methyl sulphate, makes possible a substitution in the sugar molecule concerned, although the points of maximum acidity might thereby be indicated, mixtures of dry, finely powdered potassium hydroxide and glucose in molecular proportion were subjected to the methylation process under the conditions used when treating the addition compounds. Careful study of the products of the reaction revealed that the highest yield of methylglucoside obtained by this method was never greater than 0·5%

of the weight of glucose taken, as compared with a conversion of 20% when the addition compound $C_6H_{12}O_6$,KOH was treated under the same conditions (Part I, *loc. cit.*).

<div align="center">EXPERIMENTAL.</div>

Typical Preparations of Potassium Hydroxide–Sucrose.—(1) *From octa-acetyl sucrose.* Octa-acetyl sucrose (5 g.) was moistened with absolute alcohol (10 c.c.), and a solution of potassium hydroxide (10 g.) in alcohol (50 c.c.) added. After 2 hours, the insoluble product was filtered off, washed quickly with alcohol and ether, and dried in a vacuum over phosphoric oxide (Found : KOH, by titration with $N/10$-H_2SO_4 to phenolphthalein, 31·0. $C_{12}H_{22}O_{11}$,3KOH requires KOH, 32·9%).

(2) *From sucrose.* Sucrose (5 g.), dissolved in water (7 c.c.), was mixed with alcohol until the precipitation point was almost reached; alcoholic potassium hydroxide (50 c.c., 10%) was then rapidly added, and the precipitated derivative treated as in (1) (Found : KOH, 28·1%).

The Formation of Potassium Hydroxide–Sucrose under Different Conditions.—Some indication of the amounts of potassium hydroxide taken up by sucrose under various conditions was obtained as in Part I (*loc. cit.*). A known volume of a sucrose solution in 80% alcohol was treated with a definite volume of alcoholic potassium hydroxide solution of known strength. Removal of the precipitated compound by filtration through a Gooch crucible and titration of the equilibrium solution then indicated the quantity of alkali that had been removed by the sucrose. In the case of large excesses of sucrose relative to the amount of alcoholic potassium hydroxide solution, all the alkali was removed. Therefore the solubility of the addition compounds under the conditions studied was insufficient to affect the results appreciably. Typical results are as follows :

Total concn. of sucrose, %		1·2	1·25	2·1	4·0	4·5
Concn. of KOH, N	Initial	1·24	1·33	0·96	0·22	0·08
	Final	1·14	1·22	0·80	0·03	nil.
KOH combined, %	Method (1)	46·8	49·3	42·7	26·6	10·0
	,, (2)	45·0	45·0	40·8	20·5	10·5

The results are similar to those previously recorded in the case of maltose (see Part 1), for, whilst in the more concentrated alkaline solutions the composition approximates to $C_{12}H_{22}O_{11}$,3KOH (100 g. of the disaccharide require 49·2 g. of potassium hydroxide), under less rigorous conditions $C_{12}H_{22}O_{11}$,2KOH and even $C_{12}H_{22}O_{11}$,KOH appear to exist, indicating the instability of the tripotassium derivative. It is at present impossible to decide by analytical methods whether decomposition to a mixture of sucrose and potassium hydroxide or to the lower types of addition compound takes place on washing with alcohol.

Potassium Hydroxide–Sucrose and Methyl Sulphate.—The dry compound (45 g.) prepared as in (2) was stirred with dry, neutral methyl sulphate (90 c.c.) for 10 minutes at 60° and for 5 minutes at 70—75°, at the end of which time the mass coagulated. At this point the flask was cooled, the liquid removed, and the product washed with acetone and dissolved in hot methyl alcohol (200 c.c.). On cooling, potassium methyl sulphate separated, which was filtered off, and excess of alcoholic potassium hydroxide was added, followed by ether (1000 c.c.). The potassium hydroxide derivative so isolated weighed 40 g.

Isolation of a Trimethyl Sucrose Penta-acetate.—After acidification with acetic acid and removal of the solvent, the syrup was acetylated by treatment for 2·5 hours with acetic anhydride (50 c.c.) and anhydrous sodium acetate (8 g.). The mixture was poured into water, neutralised by sodium bicarbonate, and extracted with chloroform. Removal of the solvent after drying with sodium sulphate yielded a non-reducing glass (4·8 g.). $[\alpha]_D^{20°} = +52°$ in acetone (*c*, 1) (Found : C, 50·3; H, 6·5; OMe, 15·4; $CH_3 \cdot CO$, 37·0. Calc. for $C_{25}H_{38}O_{16}$: C, 50·6; H, 6·4; OMe, 15·6; $CH_3 \cdot CO$, 36·2%).

Deacetylation and Hydrolysis of Trimethyl Sucrose Penta-acetate.—Deacetylation after Zemplén (*Ber.*, 1923, **56**, 1705) yielded a solution (60 c.c.), which was hydrolysed with oxalic acid (1 g.) at 90—100° until a constant rotation was reached (3 hours). $[\alpha]_D^{20°}$ approx. $+20°$ (*c*, 4). After neutralisation with calcium carbonate, filtration, and concentration, the syrupy mixture of methylated sugars showed $[\alpha]_D^{20°} = +19°$ in water (*c*, 1) [Found : OMe, 23·2. Calc. for $C_6H_{11}O_5(OMe) + C_6H_{10}O_4(OMe)_2$: OMe, 23·1%].

Alternative Method for isolating the Mixture of Methylated Sugars.—A more rapid method was used with success as follows. Following methylation of the dry potassium hydroxide derivative (70 g.) and the precipitation of the unchanged sucrose, the excess of potassium hydroxide was removed by the passage of carbon dioxide through the alcohol–ether solution. After removal of the precipitated potassium carbonate and evaporation of the solvent, a syrup (5 g.)

was obtained. Hydrolysis under the same conditions as before yielded the mixed methylated sugars. It was sometimes observed that, unless very large quantities of ether were employed to complete the precipitation of the potassium hydroxide addition compounds during the removal of unchanged sucrose, a small quantity of sucrose avoided precipitation, with the result that the syrup had a low methoxyl content (17%) and a low specific rotation after hydrolysis. This appeared to be due to the greater solubility of the derivatives in mixtures of methyl with ethyl alcohol. After hydrolysis, however, further treatment of the mixed sugars in ethyl-alcoholic solution with potassium hydroxide served to remove any glucose or fructose formed by the hydrolysis.

Separation of the Glucose and Fructose Fractions.—Mixtures of methylated sugars prepared as described above of methoxyl content 23% (5 g.) were dissolved in dry methyl alcohol containing hydrogen chloride (0·5 g.) and kept at 15° for 48 hours. Acid was removed with barium carbonate and after filtration the solution was evaporated. Acetylation was carried out by dissolving the product in pyridine (20 c.c.) and treating the solution with a mixture of pyridine (25 c.c.) and acetic anhydride (25 c.c.) at 70° for 20 minutes, followed by standing at 15° for 2 days. The solution was poured into water and extracted with chloroform, from which dissolved pyridine was removed by washing with dilute sulphuric acid. After removal of solvent the syrup (6·5 g.) was subjected to distillation under 0·03 mm. pressure : (1) 2·1 g. (bath temp. 145—160°), $n_D^{20°}$ 1·4470; (2) 0·5 g. (bath temp. 160—170°), $n_D^{20°}$ 1·4475; (3) 2·0 g. (bath temp. 170—180°), $n_D^{20°}$ 1·4510; (4) 0·3 g. (bath temp. 170—200°), $n_D^{16°}$ 1·4550; residue 1·7 g. Redistillation of fractions (1) and (2) appeared to yield a homogeneous product, practically the whole distilling at a bath temp. of 146°/0·04 mm.; $n_D^{16°}$ 1·4475, $[\alpha]_D^{21°}$ +24° in chloroform (*c*, 1) (Found : OMe, 30·6; CH$_3$·CO, 28·4. Calc. for $C_{13}H_{22}O_8$: OMe, 30·4; CH$_3$·CO, 28·1%). The compound would thus appear to be a dimethyl methylglycoside diacetate. On the other hand, fraction (3) showed $[\alpha]_D^{21°}$ + 33·0° in chloroform (*c*, 1·5) (Found : OMe, 19·0; CH$_3$·CO, 38·9. Calc. for $C_{14}H_{22}O_9$: OMe, 18·6; CH$_3$·CO, 38·6%). This was evidently a monomethyl glycoside triacetate.

Identification of the Fraction of High Methoxyl Content as a Derivative of 1 : 6-*Fructofuranose.*— 1·0 G. was deacetylated according to Zemplén (*loc. cit.*) and this was followed by hydrolysis in contact with *N*/10-sulphuric acid for 2 hours at 90°, during which period the rotation only fell slightly but the solution rapidly became strongly reducing. No crystalline osazone could be isolated on heating with phenylhydrazine and acetic acid in the usual manner. Two methylations with methyl sulphate (10 c.c.) and sodium hydroxide (25 c.c., 30%) (Haworth, J., 1915, 107, 8) followed and the full methoxyl content was introduced by one treatment with methyl iodide (25 c.c.) and silver oxide (4 g.) at 43° during 6 hours. After being worked up in the usual way, the product was distilled and yielded 0·6 g. of a fraction at a bath temp. of 100°/0·03 mm., $n_D^{16°}$ 1·4430, and having all the properties of tetramethyl methylfructofuranoside. This derivative was characterised by its conversion into crystalline 2 : 3 : 4 : 6-tetramethyl fructofuronamide by direct oxidation with nitric acid. The fructofuranoside (0·4 g.) was treated with nitric acid (3 c.c., *d* 1·42) for 90 minutes at 70—90°. When all action had ceased, an excess of water was added and continuous distillation with the addition of water was carried out during 6 hours. The residue was dried with benzene and esterified with methyl-alcoholic hydrogen chloride (20 c.c., 3%) for 3·5 hours. The solution was neutralised with silver oxide and after filtration and removal of the solvent was methylated with silver oxide and methyl iodide. Distillation from a bath at 135°/0·03 mm. yielded a non-reducing ester (0·3 g.), $n_D^{16°}$ 1·4430, which was converted into the amide by contact for 3 days with methyl-alcoholic ammonia. On removal of solvent the characteristic long needles appeared of the 2 : 3 : 4 : 6-tetramethyl fructo-furonamide (0·2 g.) described by Avery, Haworth, and Hirst (J., 1927, 2313). $[\alpha]_D^{20°}$ — 81° in water (*c*, 0·5), m. p. 100—101° alone or in admixture with a specimen prepared directly from tetramethyl fructofuranose (Found : OMe, 48·1; N, 5·6. Calc. for $C_{10}H_{19}O_6N$: OMe, 49·8; N, 5·6%).

Direct Oxidation of the Diacetyl Dimethyl Methylfructofuranoside.—A second portion (1·4 g.) was oxidised with nitric acid (5 c.c., *d* 1·42) for 2 hours at 70—95° and the excess of nitric acid was removed by continuous distillation with the addition of water for 24 hours. The reducing syrup obtained appeared to be the monomethyl analogue of the trimethyl lactol acid described above (Found : OMe, 14·4. Calc. for $C_7H_{12}O_7$: OMe, 14·9%).

Oxidation of the Monomethyl Lactol Acid.—A solution of the above syrup in water was acidified with *N*-sulphuric acid (11 c.c.), and the volume made up to 40 c.c. by the addition of water. This solution was titrated with 6·7 c.c. of *N*-barium permanganate. Excess of barium hydroxide was added and after some hours this was neutralised with carbon dioxide.

Filtration yielded a solution, which was evaporated (diminished pressure) to yield a barium salt (0·8 g.) [Found : OMe, 11·1; Ba, 30·3. Calc. for $(C_6H_{11}O_6)_2Ba$: OMe, 12·5; Ba, 27·7%].

Isolation of 5-Methyl γ-Arabonolactone.—Barium was removed by the addition of the calculated quantity of $N/10$-sulphuric acid and the aqueous solution was evaporated under diminished pressure to yield a glass (0·5 g.), which was heated at 90—100° for some hours (Found : C, 44·0; H, 6·4; OMe, 19·3. Calc. for $C_6H_{10}O_5$: C, 44·4; H, 6·2; OMe, 19·1%). It showed $[α]_D^{18°} + 40°$ (30 mins.); $+ 35°$ (1 day); $+ 31°$ (2 days); $+ 29°$ (8 days); $+ 27°$ (17 days, constant value); in water (c, 0·4). This slow hydrolysis is in harmony with the presence of a γ-lactone.

Identification of the Fraction of Low Methoxyl Content as a Derivative of 6-Methyl Glucose.—A portion of the fraction showing $n_D^{20°}$ 1·4510 (0·7 g.) was hydrolysed with $N/6$-sulphuric acid for 2 hours after deacetylation by the method of Zemplén (*loc. cit.*). Neutralisation with barium carbonate, filtration, concentration, and acetylation with pyridine and acetic anhydride yielded a syrup, which, dissolved in acetic acid (1 c.c.), was converted into the acetobromo-compound by contact for 2 hours with acetic acid saturated with hydrogen bromide (1·2 c.c.). The product was mixed with chloroform, and the chloroform solution washed with water and sodium bicarbonate solution, dried, and concentrated to a syrup under diminished pressure. Solution in dry methyl alcohol, followed by shaking with dry silver carbonate for 24 hours, gave rise to a non-reducing syrup, which failed to crystallise, $[α]_D^{18°} + 73°$ in chloroform (c, 2·2) (Found : OMe, 17·4. Calc. for $C_{14}H_{22}O_9$: OMe, 18·6%). Nucleation with a specimen of 4-methyl 2 : 3 : 6-triacetyl β-methylglucoside failed to induce crystallisation.

Isolation of 2 : 3 : 4 : 6-Tetramethyl Glucopyranose.—This syrup was methylated once with methyl sulphate (30 c.c.) and sodium hydroxide (70 c.c. of 30%) in the usual way, followed by treatment with silver oxide (5 g.) and methyl iodide (20 c.c.). The syrup obtained was distilled under 0·03 mm. from a bath at 100° and had all the properties of tetramethyl methylglucopyranoside. By hydrolysis for 8 hours with hydrochloric acid (5%), neutralisation with barium carbonate, concentration, and extraction with ether, crystalline 2 : 3 : 4 : 6-tetramethyl glucopyranose was obtained, m. p. 82·3° alone or in admixture with an authentic specimen. $[α]_D^{18°} + 83°$ (equil.) in water (c, 0·6) (Found : OMe, 51·8. Calc. for $C_{10}H_{20}O_6$: OMe, 52·5%).

The Reaction with Phenylhydrazine and the Isolation of 6-Methyl Glucosazone.—The remainder of the glucose fraction (1·0 g.) was deacetylated and hydrolysed as above to yield the syrupy monomethyl glucose. It was attempted to prepare 2-methyl glucose phenylhydrazone by the method of Brigl and Schinle (*Ber.*, 1929, **62**, 1716). The product, dissolved in methyl alcohol (1 c.c.), was treated with phenylhydrazine (0·6 c.c.) and a drop of glacial acetic acid at 15° for 24 hours. Removal of solvent in a vacuum, followed by nucleation with authentic 2-methyl glucose phenylhydrazone, gave rise to no crystals. A further quantity of phenylhydrazine (2 c.c.), acetic acid (3·0 c.c.), sodium acetate (10 g.), and water (30 c.c.) were added together with sodium bisulphite (1·0 g.). This mixture was heated for 3 hours at 90—100°; on cooling, an osazone separated, which was removed. A further quantity was precipitated on dilution, followed by further heating (8 hours). Total yield of crude product (0·5 g.) (cf. Helferich and Günther, *Ber.*, 1931, **64**, 1276). Several recrystallisations from aqueous pyridine raised the m. p. from 172° to 183—186°, the osazone when pure appearing in pale yellow needles. The m. p. showed no depression in admixture with a specimen of 6-methyl glucosazone prepared by the method of Helferich and Günther (*loc. cit.*), but with 3-methyl glucosazone (m. p. 179°) the m. p. was depressed to 163°. $[α]_D^{20°} - 69°$ in ethyl alcohol (c, 0·4) (Found : OMe, 8·1; N, 14·75. Calc. for $C_{19}H_{24}O_4N_4$: OMe, 8·3; N, 15·0%). The properties were thus in accord with those of 6-methyl glucosazone.

The Reaction of a Mixture of Glucose and Potassium Hydroxide with Methyl Sulphate.—Glucose (10 g.) and powdered potassium hydroxide (3 g.) which had been dried in a vacuum over phosphoric oxide were mixed with dry neutral methyl sulphate (50 c.c.) and stirred at 45° (5 mins.) and 70° (5 mins.). After the separation of the excess of glucose and acetylation (see Part I, *loc. cit.*) a syrupy acetate (0·3 g.) was obtained which was still reducing (Found : OMe, 3·0%, corresponding to 0·05 g. of methylglucoside). This was the highest yield obtained in three experiments.

Madame Curie Memorial Lecture.

DELIVERED BEFORE THE CHEMICAL SOCIETY AT THE ROYAL INSTITUTION, LONDON, ON
FEBRUARY 28TH, 1935.

By A. S. RUSSELL, M.C., M.A., D.Sc.

Some Important Dates.

1867, November 7th	Birth of Marie Sklodowska in Warsaw.
1891	Came to Paris.
1895, July 25th	Married Pierre Curie.
1897	Irène Curie born.
1904	Eve Curie born.
1906, April 19th	Pierre Curie killed in Paris.
1906	Marie Curie professor at the Sorbonne.
1934, July 4th	Marie Curie died in Haut-Savoie of anæmia.
1898, July 18th	Discovery of polonium.
1898, December 26th	Discovery of radium.
1898	Discovery of the radioactivity of thorium.
1899	Discovery of induced activity.
1903	Davy medal of the Royal Society (with Pierre Curie).
1904	Nobel Prize in Physics (with Henri Becquerel and Pierre Curie).
1911	Nobel Prize in Chemistry.
1922	Member of the Academy of Medicine of Paris.
1903	First visit to England.
1921	Ovation in the United States.
1923	Silver Jubilee of Radium in Paris.
1928	Last visit to the United States.
1929	Last visit to England.
1932	Ovation at Warsaw.
1903	Doctoral thesis " Sur les Substances Radioactives."
1910	" Traité de Radioactivité."
1921	" La Radiologie et la Guerre."
1924	" L'Isotopie et les Eléments Isotopes."

WE are here to-night to pay respect to a former Honorary Fellow of our Society and a very great woman—the greatest woman in science of our time. If ever we have a full-length, authoritative life of Madame Curie in English, I hope the story will be told with the sympathy, insight, and detachment with which Arnold Bennett traced from girlhood to the end the lives of Sophia and Constance in his great book " The Old Wives' Tale." The plain story of Marie Sklodowska—afterwards to become Marie Curie—from the early days in Warsaw, where she was born, through her struggles there and in Paris to a wide and enduring fame, with the minor ups-and-downs given their place amid the successes and the tragedy—and she did not escape tragedy and malice—till her death last summer in Savoy, should make a moving narrative. Her life, because of its connection with the wonderful flowering in physics and chemistry in the period 1896—1904, needs little help from an artist to give it interest or significance. No biographer has occasion to sentimentalise over her because she was a woman, or to make out that in her special subject in science she was first and the rest nowhere.

Marie Sklodowska, born in 1867, was the youngest of a family of five. The parents were school teachers in the capital of oppressed Poland, Warsaw. The father taught mathematics and physics; the mother, before her death when Marie was only nine, supervised a school for young girls. The old phrase " Plain living and high thinking " suffices to describe the home; it was " highbrow " in the good sense; things of the mind were thought important in it. The only brother was afterwards to become a doctor, and still practises in Warsaw. One sister studied medicine, married a Paris doctor, and now, a widow, is in charge of the Curie Radium Institution at Warsaw. A second sister became a school mistress. The eldest died comparatively young. At school Marie Sklodowska seems to have had most aptitude in mathematics, physics, and nature study. On leaving she acted for a short time as a private teacher or governess, but in 1891 she had accumulated sufficient funds to leave home and enter the Sorbonne in Paris to study afresh. There she lived in

MADAME MARIE CURIE

the economic way in which many students live, enduring hardships gladly or without comment, making study the principal thing. Various examinations were successfully passed before she began her work for her doctorate in the laboratory of Professor Lippmann. It was there in 1894 she first saw Pierre Curie. After a short visit to Poland she decided to make France her home, and in 1895 married Pierre Curie in Paris. He was 36, already distinguished for his pioneer work in magnetism and crystallography, and probably the most promising physicist working in Paris. He had just before been given a professorship at l'École de Physique et de Chimie, though with a poorly equipped laboratory and an inadequate stipend. There were no private means. The young couple started their life together in a very small way, working in the laboratory part of the day, and doing routine jobs or teaching during the rest, to eke out existence; living the happy, simple, economic, and occasionally rather anxious intellectual life, on which those who have emerged from it without bitterness or scar always look back as one of the happiest of times. The doctoral work began on the mechanical properties of certain steels, but the discovery in 1896 in a near-by laboratory by Henri Becquerel of the radioactivity of uranium, later to change the face of physics and inorganic chemistry, induced her to abandon the steels and enter the new field. Thus began her creative period, ending about 1903, when she alone or in conjunction with her husband discovered the radioactivity of thorium, found the new element polonium, discovered and isolated radium, and, generally speaking, invented radioactivity on its chemical side.

During this period, in 1897, a daughter, now Mme. Irène Curie-Joliot, destined to be hardly less distinguished in radioactivity than her mother, was born. Three years later the father was given a more remunerative post at the Faculté des Sciences, which was again bettered in 1904. Its close was marked by a visit, in 1903, of M. and Mme. Curie to London to receive, appropriately enough, the Davy medal of the Royal Society, and, in the following year, to Stockholm to get jointly with Henri Becquerel a Nobel Prize in Physics. This settled the financial position for a time. During the London visit, Professor Curie demonstrated in this very room at the Royal Institution that odd paradox—as it then seemed—the heat emission from radium at the temperature of liquid oxygen.

The years 1903 to 1911 may be taken as Madame Curie's second period. This was creatively of much less importance, but it witnessed the consolidation of most of the work done in the earlier. Polonium and radium were extracted on much larger scales, and studied by her and others both from the purely chemical and from the radioactive side. Radium became the great source of radioactive material in the research laboratories of the world, and began to find a therapeutic use in hospitals. It was prepared in the metallic state by Madame Curie and collaborators; its atomic weight was determined accurately, and its purified chloride selected as a standard of radioactivity. A good deal of miscellaneous work of permanent importance was also done. In 1904 the younger daughter was born, but in 1906 came tragedy : Professor Curie was knocked down by a lorry in Paris and killed. The widow succeeded her husband in his professorship, being the first woman professor at the Sorbonne and director of the new Radium Institute. The professorship was raised in status two years afterwards. In 1911 she again got a Nobel Prize, this time for Chemistry, and this time with no one to share it with her. After 1911 she did no work of final importance. She kept to the old paths, improved the older methods, got her data more accurate, directed research, and did much valuable work, but nothing corresponding with the discovery of radium and polonium came from it. Her attitude became protective and maternal rather than creative. She was constantly returning to the old work to meet criticism of it, to keep, so to speak, its honour bright—as, for example, in 1929, when it was seriously suggested that polonium decayed at different rates in different parts of the United States of Soviet Russia—or in seeing how her favourite elements, polonium and radium, could be of use in some discovery made by others. She continued actual work or the supervision of work till nearly the end, and never departed from the standard of the perfectly competent and interested research worker. Her last researches were with S. Rosenblum on the α-particles of varying initial velocity, emitted by different products of the actinium disintegration series.

Characteristics.

Madame Curie was about the middle height and of homely appearance. She dressed unostentatiously and, after her husband's death, generally in black. Her face was pale and not animated in repose; but for her large intelligent eyes, she would have seemed plain. She spoke quietly and with dignity but was not a ready talker. She was always willing to discuss science with those interested, provided they took the lead. Her face lit up as she spoke, and one understood the attraction she possessed for those who were interested in what she was saying. She went grey fairly early and always looked rather frail. She did everything with a quiet earnestness. Her work was part of herself. She was always unassuming and quite unspoiled by success. She was never particularly enthusiastic about the work of others when she talked, but she had no jealousy; she was in that respect uncompetitive. She was a clear and interesting lecturer in the formal manner of the French, but not a popular expositor; the ready word, the hearty manner, the eagerness to invite or continue discussion, which are the possessions of more than one of the distinguished male workers in physics of this land, were not hers. After about 1910 she learned English and eventually came to speak it well. She always had a small band of workers in her Radium Institute in Paris, but it never grew to a large school in which work was done on a very wide front; that kind of leadership happened not to be hers. She kept within a narrow field and did magnificently within it. Theoretical aspects—the study of the nucleus, for example—and mathematical treatment of physical and chemical problems did not interest her intimately. Her experimental work tended towards simplicity and straightforwardness rather than to elaboration, except perhaps when the method or the apparatus had been devised by her husband or his brother. All she did was done neatly and accurately. Her critical powers were excellent, and this is seen in her own publications as well as in all the work she directed.

Early Days of Radioactivity.*

We are doubtless tired of being told that modern physics and chemistry began with the discovery of X-rays in the November of 1895; nevertheless it is a fact. Henri Becquerel, following up this work, discovered the radioactivity of uranium in February, 1896, in an examination of the double sulphate of uranium and potassium. (How few of us know that our own Silvanus Thompson was at similar work! Claim is made for his simultaneous and independent discovery of radioactivity in his biography published in 1920.) The subject, despite its difficulty, and the small number of workers in the field, went forward rapidly, largely because there were to hand the extraordinarily delicate methods of measurement of the rays or particles, shot out by radioactive bodies, which the gaseous ionisation work of J. J. Thomson and Rutherford had developed. Becquerel showed that the radiation from uranium was common to all uranium preparations and to the element itself, and that it could both affect a photographic plate and discharge positively and negatively electrified bodies. In a way the experimental physicists were ready for all this. The α-particle had its prototype in the canal rays of Goldstein (1886), the β-particle in the electron of the discharge tube, and the non-deflectable γ-ray in the X-ray itself. The α-particle was afterwards to be identified with helium, but this new terrestrial element had been conveniently discovered by Ramsay in cleveite in 1895, and the technique of its manipulation needed little development. It is clear that these preliminary discoveries— helium, the electron, the X-ray—were the necessary precursors of radioactivity. Anybody before then could have discovered the radioactivity of uranium had he possessed either a gold-leaf electroscope or a dry photographic plate, but, in fact, he could have done little or nothing about it before 1896 because the significance of what was occurring would totally have escaped him.

But there were difficulties, and the greatest was the failure of most physicists to visualise

* Has it been pointed out before that many of the early workers had peculiar surnames or were working far from home? There were Soddy and Eve, Russ and Makower, Bragg and Kleeman, Joly and Crookes—all British, in different parts of the Empire. Rutherford was a New Zealander at Cambridge and in Montreal, Bragg a North-countryman in Adelaide, Soddy an Englishman in Canada, Madame Curie a Pole in Paris.

the atom as the simple, discrete, concrete entity we now naïvely assume it to be. It was the chemists who gave them a lead there. Physicists of the Faraday–Clerk Maxwell tradition, like Kelvin, failed for a time to distinguish in their minds atoms from molecules or, alternatively, so to theorise as to believe atoms definitely existed. Becquerel at the beginning thought radioactivity was a form of fluorescence; Stokes, President of the Royal Society, suggested it was " calorescence "; Silvanus Thompson inclined to " hyper-phosphorescence "; but these views were quickly dropped. Sir William Crookes thought that radioactive atoms might derive their energy through their peculiar ability to extract it from the surrounding gas; particles of the gas arrived at the radioactive atom with high energy and departed with low, the energy thus conveniently obtained being later emitted. As late as 1903, Kelvin suggested that the radioactive atom absorbed, not kinetic energy from a gas, but unknown radiations traversing all space, thus keeping its temperature, as was experimentally the case, above that of the surroundings, as a black body in sunshine did above that of a neighbouring white one. Different altogether were the theories of Rutherford in 1901, Perrin, 1901, and J. J. Thomson, 1903. They believed the energy of radioactivity must come somehow from within the atom. These views, in the event, were the forerunners of the complete disintegration theory of Rutherford and Soddy of 1903. To the attainment of the simple view of radioactivity that has been ours since then, Madame Curie made a most valuable contribution from the chemical side by producing the concrete fact that new radioactive elements existed. Becquerel proved in a way that radioactivity was atomic, but he did not see the importance of his results.

It was Madame Curie's great merit to have seen how important an atomic property might be, and to have made this the basis of her experimental work. She first showed that uranium preparations were radioactive, independently of their source, previous history, or chemical treatment. Using the Cambridge electrical method of measurement, she found that some uranium ores were as much as four or five times more radioactive than they should be on their uranium content. She found a mineral was not abnormally radioactive *qua* mineral; a mineral made artificially was no more radioactive than it should be. She made the correct deduction from her surprising results, namely, that pitchblende, the mineral with the most abnormal radioactivity, must contain in small amount a new radioactive substance proportionately many times more reactive than uranium itself. This supposed substance must be in small amount and new, for it was unlikely that in a well-known mineral like pitchblende any detectable quantity of a new element could be present. This location of radioactivity in concrete atoms of chemical elements was the opening move in the break-away from the abstract theories of the radioactive process of people such as Kelvin and Stokes. And it had important practical results. Madame Curie treated pitchblende just like any ordinary mixture that required a qualitative analysis : she put it " through the groups." It was fortunate that her pitchblende, containing as it did bismuth, rare earths, calcium, and barium, in addition to lead and uranium, was impure, otherwise she might have got her radioactive elements down in the wrong groups because, in absence of convenient adsorbers, their very small concentration would have kept them soluble in all precipitating reagents. Her technique was simple. She examined at every stage of the chemical work whether the radioactivity was in a precipitate or not by the ionisation method. She found in July, 1898, a new radio-element that kept with bismuth in the simple chemical operations. She called this polonium. In December she found a second, similar chemically to barium, and to this she gave the very fine name of radium. There were actually two other elements she might have found : radio-lead, the β-particle element now called radium-*D*, and actinium, the rayless body that generates the active radio-actinium. The former must have been separated from the bismuth with the lead, and the latter from the uranium with the rare earths; but neither was radioactive like polonium and radium. Their identification depended upon the growth of their radioactive products, a fact not then known, and a thing in any case which takes time. It is therefore excusable, and indeed more than excusable, that these later gleanings were not first crops.

The question how much of all this work was due to Madame Curie, how much to her husband, must arise in the minds of all of us. Who, now, could satisfy our curiosity? And does it matter very much? Some of the work was actually joint work with her

husband and with M. Bemont.   Pierre Curie was a very able man—but a physicist.   It is undeniable that Madame Curie was the chemist of the partnership; the general attack on the problem from the chemical side both in conception and in execution was hers or largely hers.   The physical measurements made by Pierre Curie were important, and his suggestions how the joint work should be done were valuable, but it was the chemical work alone that was at this stage vital.   Moreover, it is clear both from Madame Curie's doctoral thesis printed in 1903 and from Pierre Curie's work with others, that Madame Curie took a simpler view of radioactivity than her husband.   In January, 1902, they announced their view that radioactivity was an atomic phenomenon and that each atom acts as a constant source of the emission of energy.   But whether the energy was inherent in the atom, as Rutherford and J. J. Thomson thought, or collected from the surroundings and later emitted, as Crookes earlier and Kelvin later thought, they left undecided.   They postulated both views but urged neither.   There is some evidence, however, that both inclined to one side—the wrong one—and that the inclination of the husband was more pronounced than that of his wife.   That, indeed, was generally the attitude of the Paris physicists at the time. None of them was able to distinguish between the important and the trivial in experimental work, or to formulate theory like Rutherford, the young research worker of Cambridge and McGill University in Montreal; none had his imaginative power.   Whatever may be said of the pioneer workers in radioactivity, it cannot too plainly be asserted that the subject owes its remarkable development largely to one whose extraordinary insight into the ways of Nature is without parallel since the time of Newton.   It is owing to his direction that neither time nor energy was lost in the different research laboratories in following paths that would have led nowhere.

Radium.

After radium had been detected in quantities much below those capable of showing any property other than radioactivity, it was prepared in quantity—though actually only in amounts of the order of 0·1 g.—by large-scale methods.   In a mineral containing 3 kg. of uranium we now know there is present about 1 mg. of radium.   In 1000 kg. of Joachimstal pitchblende, which contained about 60% of uranium as metal, there were present about 200 mg. of radium.   The Austrian government generously gave Madame Curie a ton of uranium residues from the Joachimstal mine, and scientific societies and private individuals helped financially to defray the cost of the long and laborious work of separation; but the principle was simple : she merely had to keep her eye on the barium.   Whatever were the . impurities, whatever chemical operations were carried out, the radium always cleaved to the barium, eschewing all else.   She got first about 20 kg. of barium salts about 30 times as radioactive as uranium itself, and then 8 kg. about 60 times as radioactive.   From this, radium was purified by fractional crystallisation of chlorides, the radium chloride being much the less soluble.   The process was followed by the electrical method, by the spectroscope, and, at times, by eye.   (Crystals of radiferous barium were at first colourless, in a few hours they became yellow, and later became orange or even rose-red.   The rapidity of this coloration was a function of the barium present, and a maximum for a definite proportion of radium and barium.)   In those days spectroscopic evidence was considered more convincing than radioactivity as evidence of a new element; for what eventually was called radium might have turned out to be just some induced or modified form of barium. Becquerel, indeed, who was, like Madame Curie, in Paris, was committed to an induction theory of radioactivity and was a powerful influence.   Madame Curie's work made nonsense of such a view.   New spectrum lines were revealed as soon as there was one part of radium in about 8000 of barium.   The long crystallisation process, which could have been greatly shortened had she used the bromide instead of the chloride, eventually gave her several hundred milligrams of nearly pure radium chloride.   Atomic-weight determinations of the increasingly pure material, then rightly the criterion of chemical respectability, rose from 137, through 146 and 175, finally to 225, attained with 90 mg. of chloride in 1902.   There was no doubt that radium was a new, completely definite, alkaline-earth element with a place awaiting it in the Periodic Classification; when atomic numbers were allotted a decade later, it was given 88.

By 1907 she had repeated the work with 400 mg. of radium chloride and obtained the value 226·2 (subsequently recalculated to 226·4). The reaction was $RaCl_2 : AgCl$, silver being taken as 107·8 and Cl as 35·4. The increase of more than a unit could not wholly be ascribed to increase in purity of the salt; it was due to better reagents and vessels, and to the accuracy which could be attained with more reasonable amounts of material. This time there was not more than 0·1% of barium in the radium. In 1910 Madame Curie and Debierne isolated pure radium metal by the electrolytic method of Guntz. They used a platinum–iridium anode, 10 g. of a mercury cathode, and an aqueous solution of radium chloride equivalent to about 100 mg. of the metal. The electrolysed radium amalgamated easily. Mercury was removed by distillation in hydrogen; a brilliant white metal which melted sharply at 700° remained. This metal behaved chemically as befitted its place in the Periodic Classification. It decomposed water, formed a very soluble hydroxide, and a black nitride (presumably of formula Ra_3N_2) insoluble in water, easily decomposed by hydrochloric acid. The metal was much more volatile than barium, being closer to calcium in volatility. It was not anticipated that any startling results would emerge from this work; it was merely an experiment in manipulation, worth doing once. The fractional sublimation of the metals in a vacuum as a possible means of ridding the radium of barium was the only new point of chemical interest.

On the recommendation of an International Committee which met in Brussels in 1910, Madame Curie prepared a radium standard, sealed in a thin glass tube, of 21·99 mg. of the pure radium chloride used by her in the determination of the atomic weight. The source of the radium was uraninite, containing only a trace of thorium, from St. Joachimstal. Meanwhile, Professor Otto Hönigschmid had prepared three specimens of radium chloride, weighing 10·11, 31·17, and 40·43 mg., from the radium whose atomic weight he had found to be 225·95. In 1912 the specimens were compared carefully. The Paris and the Austrian standard agreed within the errors of measurement (which were definitely not greater than 0·3% and probably much less). 31·17 Mg. on the Austrian standard was 31·24 on Madame Curie's; 10·11 was 10·13. As the standards were entirely independent, the agreement was a testimonial to the care and accuracy of Madame Curie and of Professor Hönigschmid. Madame Curie's standard became the International Radium Standard which has since been preserved at the Bureau des Poids et Mesures at Sèvres, near Paris. The 31·17-mg. Austrian standard, kept at the Academy of Sciences in Vienna, became a reserve standard.

The accepted value of the atomic weight of radium—that of O. Hönigschmid, 225·95—we now believe, from the general results of F. W. Aston, to be low. Those results indicated that 226·1 is a likelier value. If this be so, Madame Curie's value is not so far out as it seems. At a Conference in Brussels in 1910, a new unit of radioactivity, the Curie, was decided upon, *viz.*, the amount of any product in the uranium–radium disintegration series in equilibrium with 1 g. of radium element. The name was chosen in honour of Pierre Curie. In the discussion it was strongly urged by some members that the Curie would be more suitable for use if it were merely a thousandth of what ultimately it was fixed to be; for, in 1910, a gram of radium was a legendary amount, many laboratories made shift with fractions of a milligram, and the sensitivity of instruments, as well as rarity and cost, encouraged the use of small amounts. The logical French mind, however, wished to identify the new unit with the unit of mass, the gram, and not, for mere convenience, with a fraction of it. The suggestion that the Curie should be what now is a millicurie, however, prevailed in the committee (which included Madame Curie) and was temporarily adopted. But after that meeting she must have thought what a poor miserable thing the new unit was going to be, a mere thousandth of what she had hoped! It did not seem proper that such a thing should bear her husband's name. So next day the Curie was fixed as she desired—a thousand times the original suggested value. To-day, as a consequence, despite the amounts of radium now available, we still struggle with terms like " millicurie," " microcurie," and even " millimicrocurie."

Polonium.

Polonium was precipitated with bismuth, from which Madame Curie effected a partial separation of it by purely chemical methods. The chemical work was less clear-cut; at

first she doubted if polonium was of the same class of radioactive substance as radium. There was an outside possibility that the activity of polonium was entirely induced by the proximity of substances themselves radioactive—in which case it would have to be agreed that polonium had the power of acquiring atomic activity semi-permanently. There was, secondly, a possibility that, while the activity of polonium was inherent, it might be spontaneously destroyed under some conditions other than those obtaining in the ore (where, of course, it was not destroyed). No opinion could then be given. About this time, W. Marckwald concentrated the polonium (which he called radiotellurium) by dipping a rod of bismuth into a hydrochloric acid solution of the radioactive bismuth obtained from pitchblende residues. He also effected a notable separation with stannous chloride. From the first, Madame Curie noticed that the radioactivity of this substance, unlike uranium, unlike thorium, unlike radium, was not permanent but decayed steadily with lapse of time. Marckwald thought at one time that Madame Curie's product was a mixture giving β-rays as well as α-particles, and could not understand, being what it was, why it resembled bismuth chemically so much as she said. He had doubts also whether it decayed with time. His preparation and her polonium were identical, however, in emitting α-particles which were easily absorbed by matter, and by 1906 there was no doubt of their identity in the pure states. Polonium or radiotellurium was the top member of Group VIB of the Periodic Classification which included selenium and tellurium; this missing element was afterwards to be given the atomic number 84, and was shown, just as much as radium, to be an element, despite the minute amount of it available—despite, also, its decaying to half-value in the short period of 140 days.

By 1910 Madame Curie and M. Debierne had isolated as much as 2 mg. of polonium estimated to be nearly 5% pure—then a remarkable achievement of chemical skill and pertinacity. From about 2 tons of uranium mineral, 200 g. of residue were concentrated, having, weight for weight, an α-particle activity 3500 times that of uranium, the whole of the activity being due to polonium. This was concentrated by chemical methods to 1 g., and found to have traces of mercury, silver, tin, gold, palladium, rhodium, lead, zinc, barium, calcium, and aluminium. The gram was concentrated to 2 mg. by electrolysis, of which 0·1 mg. was thought to be polonium. This preparation contained new spectral lines, and it was hoped that, as they diminished in intensity with the decay of the polonium, those of lead would take their place. The result of this hope seems not to be recorded. It was at that time fairly certain that lead was the end product of the uranium–radium series and the direct product of polonium, yet it did not then occur to Madame Curie, or to anybody who expressed himself in print, that the atomic weight of that lead must be abnormal in being at least one unit below the accepted value for ordinary lead, 207. Later, in 1913, when the importance of this discrepancy had been pointed out by others, she worked on the atomic weights of different leads, finding low, though not minimal, values for uranium-lead, and high, though not maximal, values for thorium-lead, but these results came too late to give to the developing subject the impetus the earlier observations might have done.

Induced Activity.

The Curies in Paris in 1899 for radium, and Rutherford at McGill in 1900 for thorium, independently discovered the phenomenon which began to be known as " excited " or " induced " activity; that is, they observed that every substance which remained near a radium or thorium preparation became in time itself radioactive. Rutherford suggested in explanation that thorium and possibly other radioactive bodies generated what he called an emanation or gaseous material which, first, by moving about, and secondly, by in some way producing particles of radioactivity, accounted for excited activity. The latter radioactivity was material; it was dissolved by some acids and not by others; it could be rubbed off by the finger or by sand-paper. The explanation he gave then is that which is now accepted. The Curies, however, took another view. They considered it beyond dispute that their preparations of radium could neither sublime nor otherwise distil at the ordinary temperature on the surfaces where the excited radioactivity made its appearance. And they could not accept at first the view that the emanation was real and material.

There was no spectroscopic evidence of the gas they found; moreover, it was patent that in time it disappeared even when kept in a sealed vessel. The view of the emanation, stated unambiguously by Madame Curie in her thesis, was that it was only a form of radioactive energy stored in the surrounding gas in a form hitherto unknown. Logically, it followed that the excited activity could not be material, and hence it was thought to be, and called, " induced." The crux of the matter was the nature of the emanation. If it were a gas, there was obviously a mechanism of transport of radioactive material independent of the sublimation or distillation of the very solid particles of radium or thorium preparations. The decisive experiment—sealing up the radium—soon decided which school of thought was right, but the positiveness of both the Curies on the stored-up-energy theory of the emanation, and the fact that their neighbour Becquerel was committed to an induction theory of radioactivity, carried them away from the simple, concrete view which was after- wards to triumph so magnificently. Madame Curie was soon to accept the material theory of excited radioactivity, but she and the French school continued to use " induced activity " as a term for several years afterwards. The jargon of those days—" induced activity," " excited activity," " emanation "—suggests that the very early attitude to those experi- mental facts was not unlike that towards some mysterious thing like mesmerism or hypnot- ism where " emanations," " passes," " excitations," and " inductions " have always been common form. There is little doubt that the understanding of the cause and nature of radioactivity was retarded by the fixed idea held then in Paris that radioactivity was an unchanging phenomenon, not something which decayed with time. It was an argument against the real nature of the emanation that it disappeared in time. To us now, of course, this disappearance is no difficulty. As the gaseous matter decays, so are produced the solid particles of radioactivity which all the dispute had been about. But that view had yet to be put forward; it awaited the classical work of Rutherford and Soddy in 1902— 1903. Moreover, it was not a final fact that the radium emanation when kept in a sealed vessel decayed to nothing. The Curies themselves were the first to find evidence of the existence of " active deposit of slow-change " (now called radium-D, -E, and -F), which remained after the radium emanation and its "quick-changing products " had ceased to be detectable.

The Second Period.

After the initial creative impulse, at its height between 1897 and 1903, had spent itself about 1910, Madame Curie was content to keep the old work going, to further all the scientific interests she had acquired in the creative period, and, as was said above, to keep untarnished the honour of both the facts and the theories of radioactivity in which she had interest; her work became secondary, not creative. When Sir William Bragg showed, in 1904, that the ionisation produced by the α-particles from radium and its short-lived products extended into the gas a well-defined distance—the range—and then abruptly ended, Madame Curie was able at once to confirm this phenomenon for the simpler α-particles from her radio-element polonium. In 1908, an extraordinary series of observ- ations emanated from the chemical laboratories of Gower Street. Copper and its salts were supposed by Sir William Ramsay and A. T. Cameron to be disintegrated by the radium emanation into such alkali metals as potassium, sodium, and lithium. Elements can now be disintegrated by α-particles and other atomic projectiles, but that work was in no sense an anticipation of this. Madame Curie and Mlle. Gleditsch, concentrating chiefly on lithium, were unable to confirm that work; they traced the alkali metals to impurities in the vessels and reagents used, and rendered it probable, though not certain, that this accounted for all the observations of Ramsay and Cameron. In 1911 actinium, which had been discovered by Madame Curie's methods by Debierne in Paris in 1899 and till then regarded as a long- lived element, was found by Madame Curie to have a half-period of the order of only 20 years. This result raised the important question, happily now solved, why its production from uranium—a necessary consequence of its short period—had not been experimentally observed. In 1913 she made a defensive contribution to an idea that was periodically being attacked, namely, that the rate of decay of a radioactive body was quite independent of temperature, concentration, pressure, or even geography. With Kamerlingh Onnes

she showed that immersion of a strong radium source in liquid helium for 90 minutes did not affect the penetrating γ-radiation by 0·1%, and probably by not more than 0·02%, of its activity at the ordinary temperature.   And one of the last pieces of work she did was to criticise destructively a series of experiments made in Russia, where it was alleged that her own element polonium disintegrated at different rates in different parts of that land— capriciously, for there was found no general correlation between latitude and rate of decay. Happily, the preparation conformed to the accepted value of the half-value period in the two great cities of Moscow and Leningrad.   There are, of course, no such real variations. The results were seriously put forward and equally seriously rebutted, but workers in the future may be permitted to regard the episode as a jest : Russia chaffing Poland on a sensitive point.

The War.

The War rightly interrupted Madame Curie's purely scientific work, but not, of course, her activities.   The " Union des Femmes de France," one of the three French Red Cross societies, gave her the management of its X-ray service.   Another, the " Patronage National des Blessés " got her to establish installations wherever they were urgently needed.   Later, Madame Curie, acting with the " Service de Santé," créated a school of radiology for nurse-specialists, which from 1916 till the close of the War achieved success. She served on many committees.   The prestige of her name (and in war time great names had great value), as well as her actual services, was invaluable to her adopted country during that very difficult period.   In a little book published in 1921 she gave an account of the X-ray and radium-therapy services with which she had been connected during those years.

After the War.

In so far as a worker in science can be a world figure, Madame Curie was a world figure. The concrete discovery of new elements that had surprised the world of science by their oddness and were giving hope of being of decisive value in the cure of cancer, and the fact that she was a woman, later to be widowed in tragic circumstances, all helped to bring her name to the attention of the ordinary person.   She had come as an obscure person to Paris from Warsaw, and by pure merit, without any kind of influence, had attained a position which had twice been crowned by the Nobel Prize.   Her first visit to the United States in 1921 was like the visit of a queen.   On that occasion she was given a gram of radium, which had been subscribed for in her honour, by the women of America.   The presentation was made her at the White House by the President himself, the unfortunate Harding, in a well-phrased speech.   In her adopted country, in Paris on the 25th anniversary of the discovery of radium, in December, 1923, she was the centre of a great gathering of French notabilities, with the President at their head.   A pension of 40,000 francs a year was then settled on her and her daughters.   Later, in 1932, all Poland with their President received her like royalty as she attended the opening of the Curie Radium Institution in her native Warsaw.   The little teacher who had left Poland in the early 'nineties with her hard-won savings to renew her study in the great French capital then returned in triumph.   No praise is so sweet as that of those who knew us when we were young, unknown, and immature.   What contrasts must have presented themselves to her !   What thoughts must have passed through her mind as she recalled all that had happened to her, to her relations and friends, and to her loved country during those forty years !   The whirligig of time had brought its change, yet it had not spoiled the essential woman in her.

As her scientific work eased in the years after the War, that of her elder daughter became more and more energetic.   The tragedy that had entered Madame Curie's life and partly crippled her work—the loss of her husband—had some compensation in the promise of this daughter.   Like her mother, the daughter had been brought up in a home where both parents had had at times to practise economy.   Like her mother, she was in time to marry one of the most promising physicists in Paris.   Like her mother, she was, with her husband, to make a discovery—the artificial radioactivity of the light elements—of immense import- ance and promise in the subject of atomic physics.   We in science are the last to suggest that history repeats itself, but these similarities in mother and daughter are just worth

noting. Madame Curie was the only person ever to get a Nobel Prize twice, though not, of course, the only one to deserve the double honour. It seems likely—it is, indeed, very probable—that in due time daughter and son-in-law also will partake of this emolument. When they obtain it, a family record will be established in prizes as remarkable as deserved.

It does not detract from Madame Curie's greatness to say as a last word that she was fortunate. She was fortunate in being in Paris, and in being there at just the right time. She was fortunate in being married to Pierre Curie, and in being a conscientious, hard-working, clear-thinking chemist when physicists were plentiful and chemists both rare and essential. It was well also, I think, that she was not too clever at a time when mere cleverness was some bar to original thought. She had assuredly a great opportunity, but she had the brains and the courage to seize it, and tenaciously to retain it.

" Radium," " Polonium," the " Curie " are words for all time. They will rightly keep Madame Curie's name alive as long as science lasts.

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146. *Synthetical Experiments on Protopine and Allied Alkaloids. Part II. New Synthesis of the Berberine Ring-system, and of a Ring-homologue of the Aporphine Alkaloids.*

By Thomas S. Stevens.

The work now described was commenced in 1925, in parallel with the researches of Haworth and Perkin which finally led to the synthesis of cryptopine and protopine (J., 1926, 1769). The first objective was the preparation of the dihydroberberine analogue (I), the readily obtainable substance (II) being used as the starting point, so that the methods elaborated might be available for application to actual alkaloid syntheses involving less accessible initial materials.
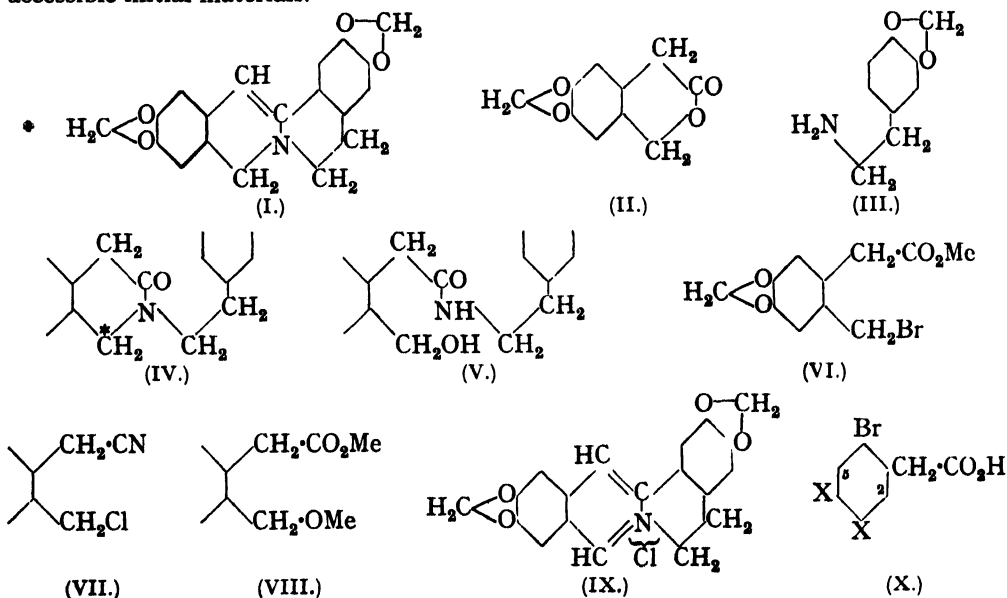
The series of reactions (II) + (III) ⟶ (IV) (compare the production of phthalide-anil from phthalide and aniline) ⟶ (I) was investigated, but the first step led only to the *hydroxy-amide* (V). The *lactam* (IV) was, however, obtained by the action of (VI) or (VII) upon (III), followed in each case by hydrolysis, but its dehydration to (I) could not be effected. Haworth, Perkin, and Pink (J., 1925, **127**, 1709) were similarly unable to dehydrate homophthalimides (as IV, with CO in place of $\overset{*}{C}H_2$).

The *methyl* ether of (V), prepared from (VIII) and (III), when treated with phosphorus pentachloride, underwent a double ring-closure, with elimination of water and methyl alcohol and simultaneous dehydrogenation, to give a 25% yield of the berberine analogue (IX), which has already been described by Buck, Perkin, and Stevens (J., 1925, **127**, 1462). A formal proof is thus supplied of the correctness of the orientations assigned to the berberine derivatives described in that paper. The same product (IX) was similarly obtained, in smaller quantity, from (V) itself. This synthesis of berberine derivatives is simpler, but less flexible, than that used by Haworth and Perkin (*loc. cit.*). Numerous unsuccessful attempts were made to condense formaldehyde with bromohomopiperonylic or bromohomoveratric acids (X : XX = CH_2O_2 or 2OMe) and their derivatives in order to obtain analogues of (II) suitably oriented for actual alkaloid syntheses. Here it was necessary that the entrant group should take up position 2; the alternative position 5 might have led to the synthesis of (XVII) (*vide infra*).

An attempt to prepare (I) from (V) by the action of phosphorus oxychloride yielded a product which could not be purified, but gave the colour reactions of a benzyldihydro-*iso*quinoline. Reduction produced a crystalline secondary base " A " whose analytical data were in better agreement with the formula $C_{19}H_{17}O_4N$ (XII) than with $C_{19}H_{19}O_4N$ (XI).

(XI.)   (XII.)   (XIII.)
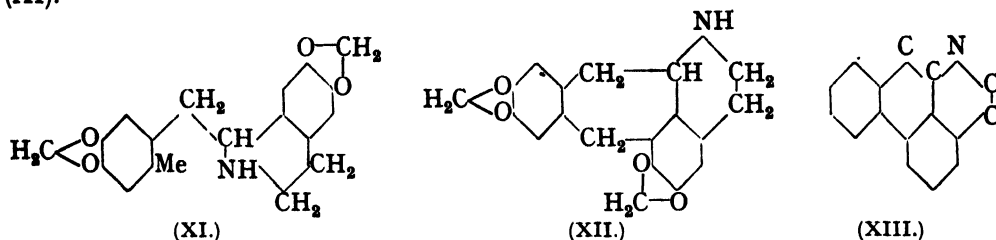
These are the only formulæ which can be ascribed to " A " with any degree of probability, and (XI) has been excluded by the following synthesis :

(XI)
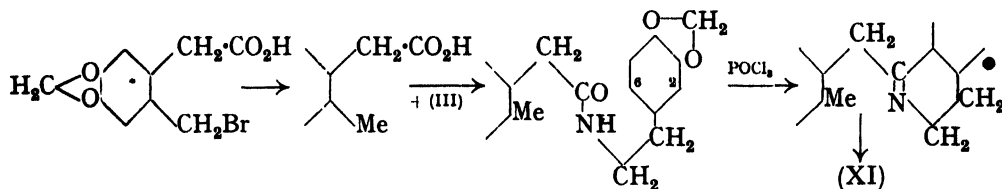
(The product was distinct from " A "; the assumption of ring closure at position 6 rather than at position 2 is supported by numerous analogies.) The remaining alternative (XII) contains the apomorphine skeleton (XIII), modified by the presence of an extra methylene group in the central ring.

Degradative and synthetic experiments designed to confirm the structure attributed to " A " met with very limited success. The base lost its nitrogen at the second stage of exhaustive methylation; the resulting unsaturated compounds yielded no homogeneous product on oxidation.

(XIV.)   (XV.)
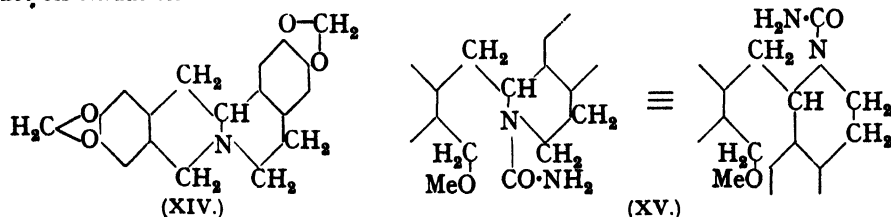
Conversion of (XIV) by successive action of cyanogen bromide, sodium methoxide, and sodium hydroxide into (XV), followed by treatment of the latter with phosphorus oxychloride, and hydrolysis, appeared to yield " A," but the small quantity obtained could

not be identified with certainty. The preparation of derivatives of " A " by condensation of (XVI; R = Me or SO₂Ph) with formaldehyde failed, as did attempts (see experimental part) to prepare (XVII) as initial material for a more elaborate synthesis.

(XVI.)   (XVII.)   (XVIII.)
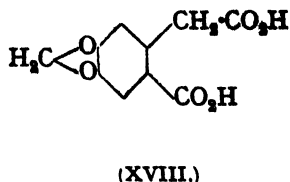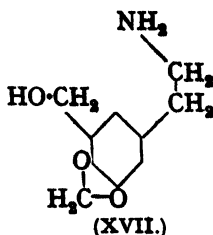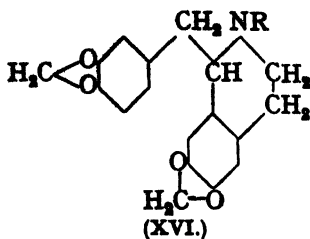
It was incidentally observed that 6-carboxyhomopiperonylic acid (XVIII) yields 6-bromohomopiperonylic acid when treated with bromine water (compare Jones and Robinson, J., 1917, 111, 909).

EXPERIMENTAL.

6-Hydroxymethylhomopiperonoyl-β-piperonylethylamine (V).—Equimolecular quantities of β-piperonylethylamine and the lactone (II) (Stevens, J., 1927, 178) were refluxed in benzene for 3 hours, and the solid, recrystallised from alcohol, formed white needles, m. p. 176°, sparingly soluble in alcohol or xylene (Found : C, 63·8; H, 5·4; N, 3·8. C₁₉H₁₉O₆N requires C, 63·9; H, 5·3; N, 3·9%). The same product resulted when the base and the lactone were heated alone at 180—200°; higher temperatures led to decomposition.

*3-Keto-6 : 7-methylenedioxy-2-β-piperonylethyl-1 : 2 : 3 : 4-tetrahydro*isoquinoline (IV).—The nitrile (VII) (Stevens, *loc. cit.*) (1 mol.) and β-piperonylethylamine (2 mols.) were boiled for 2 hours in benzene, water added to dissolve the solid, and the product precipitated as hydrochloride by hydrochloric acid. *6-β-Piperonylethylaminomethylhomopiperonylonitrile*, liberated by ammonia and extracted with chloroform, crystallised from ligroin in needles, m. p. 77—79° (Found : C, 67·3; H, 5·5. C₁₉H₁₈O₄N₂ requires C, 67·5; H, 5·3%). When treated with hydrogen peroxide and alkali in aqueous-alcoholic solution, it yielded the lactam (IV), which was more advantageously prepared as follows : The ester (VI) (Stevens, *loc. cit.*) (1 mol.) was heated for a short time with β-piperonylethylamine (2 mols.) in benzene, excess of alcoholic potash added, and the whole boiled for 2 hours and poured into excess of boiling 10% acetic acid. The substance (IV) was extracted from the resulting solid by hot alcohol or aqueous acetic acid, and crystallised from benzene–ligroin in pale yellow needles, m. p. 144—146° (Found : C, 67·0; H, 5·5. C₁₉H₁₇O₅N requires C, 67·2; H, 5·1%). It resisted the known methods of cyclisation and was mostly recovered unchanged even after fusion with phosphoric oxide at 150°. The residue from the extraction of (IV) was acidic, crystallised from acetic acid in microscopic laminæ, m. p. 225—232° (decomp.), and was evidently *bis-(6-carboxymethyl-homopiperonyl)-β-piperonylethylamine* (Found in material dried at 100° : C, 63·3; H, 5·1. C₂₉H₂₇O₁₀N requires C, 63·4; H, 5·0%).

Synthesis of 2 : 3 : 10 : 11-Bismethylenedioxyprotoberberinium * *Chloride* (IX).—6-*Methoxy-methylhomopiperonyl-β-piperonylethylamine*, prepared by heating equimolecular quantities of β-piperonylethylamine and methyl methoxymethylhomopiperonylate (VIII) (Stevens, *loc. cit.*) for 3 hours at 170°, and crystallised first from methyl alcohol and then from benzene–ligroin, formed a microcrystalline powder, m. p. 103—105° (Found : C, 64·4; H, 6·0; OMe, 8·2. C₂₀H₂₁O₆N requires C, 64·7; H, 5·7; OMe, 8·4%). It was dissolved, with excess of phosphorus pentachloride, in chloroform, and kept in a warm place for several days. The basified mixture was extracted with chloroform, from which a crude picrate was precipitated; the portion of this which dissolved only sparingly in acetic acid was treated with benzene and hot hydrochloric acid, and the berberinium chloride was collected after cooling (Found : Cl, 8·7. Calc. for C₁₈H₁₄O₄NCl,2H₂O : Cl, 9·0%). The substance was identified with that prepared by Buck, Perkin, and Stevens, by direct comparison of the chlorides, bromides, and picrates, and by reduction (zinc and sulphuric acid) to the corresponding tetrahydroberberine, m. p. and mixed m. p. 214°.

Substance " A."—Phosphorus oxychloride (6 c.c.) was added to the amide (V) (3 g.) sus-

* See Buck, Perkin, and Stevens (*loc. cit.*) for numbering of protoberberine, and protopapaverine. The name protolaudanosine is used analogously.

pended in boiling toluene (80 c.c.). The solid quickly dissolved, and after 1 hour's boiling, ligroin was added to the cooled solution and the solvents were decanted from the gummy phosphate. When the latter was dissolved in aqueous alcohol and treated with alkali, a yellow solid was obtained, which rapidly turned brown in the air, and then formed yellow salts and gave a green coloration on boiling with acetic anhydride (compare Buck, Haworth, and Perkin, J., 1924, **125**, 2180). The phosphate was dissolved in hot dilute sulphuric acid and reduced with zinc dust; the resulting, sparingly soluble sulphate yielded the base " A " (6 : 7 : 3' : 4'-*bismethylenedioxy*-8 : 6'-*methylene*-1 : 2 : 3 : 4-*tetrahydroprotopapaverine*), which, repeatedly crystallised from alcohol, formed needles, m. p. 188° (Found : C, 70·8; H, 5·3; N, 4·4; *M*, Rast, 335. $C_{19}H_{17}O_4N$ requires C, 70·6; H, 5·3; N, 4·3%; *M*, 323). The nearly colourless solution in concentrated sulphuric acid gave with a crystal of potassium nitrate an intense brownish-purple coloration, which slowly faded to yellow. The p-*nitrobenzoyl* derivative, prepared in warm pyridine, crystallised from much acetic acid in clusters of minute, pale yellow, prismatic needles, decomp. 285° (Found : C, 65·8; H, 4·5. $C_{26}H_{22}O_7N_2$ requires C, 66·1; H, 4·3%). The benzenesulphonyl derivative, similarly obtained, crystallised from benzene–alcohol in irregular prisms, m. p. 215—218°.

Exhaustive Methylation.—Methyl sulphate and sodium carbonate were added in moderate excess to a suspension of the base " A " in boiling methyl alcohol. The base quickly dissolved, and after 1 hour's heating the acidified and concentrated solution was treated with solid potassium bromide. 6 : 7 : 3' : 4'-*Bismethylenedioxy*-8 : 6'-*methyleneprotolaudanosine methobromide* was precipitated, and formed cream-coloured rectangular laminæ from water, m. p. 210—220° (decomp.) (Found : Br, 17·5; loss at 130°, 3·8. $C_{21}H_{22}O_4NBr,H_2O$ requires Br, 17·7; loss, 4·0%). Heated for 2 hours on the water-bath with excess of methyl-alcoholic potash, it yielded 6 : 7 : 3' : 4'-*bismethylenedioxy*-8 : 6'-*methyleneprotolaudanosine methine*, which was purified through the sparingly soluble *hydrochloride*, minute leaflets, m. p. 170—174° with previous softening (Found : HCl, 9·0. $C_{21}H_{21}O_4N,HCl$ requires HCl, 9·4%). The free base formed needles from ligroin, m. p. 101° (Found : C, 71·5; H, 5·9; equiv., 351. $C_{21}H_{21}O_4N$ requires C, 71·8; H, 6·0%; equiv., 351). The *methobromide*, prepared *via* the methosulphate, crystallised from water in small needles, which softened from 210° and decomposed at 265° (Found : Br, 16·9; loss at 130°, 7·0. $C_{22}H_{24}O_4NBr,2H_2O$ requires Br, 16·6; loss, 7·5%). The nitrogen-free compound formed on treatment with alkali was amorphous and presumably polymerised.

Synthesis of 6 : 7 : 3' : 4'-*Bismethylenedioxy*-6'-*methyl*-1 : 2 : 3 : 4-*tetrahydroprotopapaverine* (XI).—A solution of the lactone (II) in acetic acid–hydrobromic acid was kept for some hours and reduced with zinc dust at 80°. A chloroform extract of the filtered, diluted, and acidified (hydrochloric) mixture yielded to sodium bicarbonate solution 6-*methylhomopiperonylic acid*. This formed small prisms from benzene, m. p. 148—151°, which was sparingly soluble in water (Found : C, 62·0; H, 5·3. $C_{10}H_{10}O_4$ requires C, 61·8; H, 5·2%). Heated at 190° for 2 hours with a slight excess of β-piperonylethylamine, it gave 6-*methylhomopiperonoyl*-β-*piperonylethylamine*, needles from alcohol, m. p. 158—160° (Found : N, 4·2. $C_{19}H_{19}O_6N$ requires N, 4·1%). This amide was cyclised and reduced as described for the preparation of " A " above; after liberation with ammonia and extraction with chloroform, the base (XI) crystallised from benzene–ligroin in minute needles, m. p. 92—94° (Found : equiv., 328. $C_{19}H_{19}O_4N$ requires equiv., 325). The *picrate* formed deep orange prisms from much acetic acid, m. p. 240° (decomp.) (Found : C, 54·5; H, 3·8. $C_{19}H_{19}O_4N,C_6H_3O_7N_3$ requires C, 54·2; H, 4·0%).

Synthesis of " A " *from Bismethylenedioxytetrahydroprotoberberine.*—Excess of cyanogen bromide was added to a suspension of the base (XIV) in hot benzene, and the mixture kept at 70° for 3 hours. The solvent was distilled, and the residue heated for ¼ hour with excess of methyl-alcoholic sodium methoxide and for 1½ hours more after addition of water. The acid-soluble material, a weak base, formed leaflets from methyl alcohol, m. p. 75—80° (unchanged by repeated crystallisation), and was probably 6 : 7 : 3' : 4'-*bismethylenedioxy*-2-*carbamyl*-6'-*methoxymethyl*-1 : 2 : 3 : 4-*tetrahydroprotopapaverine* (XV) (Found : N, 6·9, 7·0. $C_{21}H_{22}O_6N_2$ requires N, 7·0%). It was boiled for 1½ hours with phosphorus oxychloride in toluene, treated with alcohol and sodium hydroxide solution, and the product extracted with chloroform and boiled for 4 hours with butyl-alcoholic potash. A small quantity of basic material resulted, which, after recrystallisation, melted at 175° alone or mixed with " A," and gave the colour reaction of that substance. Alteration in conditions did not improve the yield, and lack of material prevented repetition on a large scale.

6 : 7 : 3' : 4'-*Bismethylenedioxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydroprotopapaverine* (XVI; R = Me) was prepared by refluxing the crude product of cyclisation of homopiperonoyl-β-piperonylethylamine (Buck, Perkin, and Stevens, *loc. cit.*) in benzene with excess of methyl sulphate,

and reducing the gummy methosulphate with zinc dust and dilute sulphuric acid; the resulting sparingly soluble sulphate was recrystallised from alcohol–ether. The *picrate*, orange-yellow prisms from much acetic acid, decomposed at 210° (Found : N, 9·9. $C_{19}H_{19}O_4N,C_6H_3O_7N_3$ requires N, 10·1%). 6 : 7 : 3′ : 4′-*Bismethylenedioxy-2-benzenesulphonyl-1 : 2 : 3 : 4-tetrahydro-protopapaverine* (XVI; R = SO₂Ph), prepared from the secondary base (Buck, Perkin, and Stevens, *loc. cit.*) in warm pyridine–benzene, formed long rectangular laminæ from benzene, m. p. 110—113° (Found : N, 3·4. $C_{24}H_{21}O_6NS$ requires N, 3·1%).

Attempts to prepare (XVII).—*Aceto-6-bromo-β-piperonylethylamide*, from the amine (Stevens, *loc. cit.*), formed needles, m. p. 125°, from aqueous methyl alcohol (Found : N, 4·9. $C_{11}H_{12}O_3NBr$ requires N, 4·9%). This amide, and 6-bromohomopiperonylic acid (X) and its nitrile and methyl ester, were separately treated with formaldehyde under a variety of conditions in the hope that the group –CH₂·OH might enter. in position 5, but this could not be effected. 6-Bromohomopiperonylic acid, obtained by bromination of homopiperonylic acid in warm acetic acid, was identical with material prepared from 6-bromopiperonal according to Girardet (*Helv. Chim. Acta*, 1931, 14, 514). The *methyl* ester crystallised from methyl alcohol in needles, m. p. 84° (Found : Br, 29·1. $C_{10}H_9O_4Br$ requires Br, 29·3%), and with methyl-alcoholic ammonia at 130° yielded the *amide*, needles from much benzene, m. p. 181° (Found : Br, 31·2. $C_9H_8O_3NBr$ requires Br, 31·0%). The amide (1 g.), phosphorus oxychloride (2 c.c.), and toluene (5 c.c.) were boiled for 2¼ hours, poured into sodium carbonate solution, and the *nitrile* extracted with chloroform; it formed long prisms from aqueous methyl alcohol, m. p. 65—67° (Found : Br, 32·7. $C_9H_6O_3NBr$ requires Br, 33·2%). The same substance was prepared from 6-bromopiperonylpyruvic acid (Girardet, *loc. cit.*) *via* the *oxime* [minute prisms from aqueous alcohol, m. p. 166—167° (decomp.) (Found : N, 5·0. $C_{10}H_8O_5NBr$ requires N, 4·6%)], as described by Edwards for the bromine-free analogue (J., 1926, 744).

Action of Bromine Water on 6-Carboxyhomopiperonylic Acid (XVIII).—The acid, dissolved in the least possible quantity of sodium carbonate solution, was treated with excess of bromine water. The first additions caused a deep blue coloration, which gave place to a yellowish precipitate; further gradual addition of carbonate restored the coloration and finally gave a clear dark solution, from which 6-bromohomopiperonylic acid (mixed m. p.) was obtained.

147. *Synthesis of Cholanthrene.*

By J. W. COOK, G. A. D. HASLEWOOD, and (MRS.) A. M. ROBINSON.

THE most potent carcinogenic compound so far encountered is methylcholanthrene, a transformation product of the bile acid, deoxycholic acid (Cook and Haslewood, J., 1934, 428; Barry, Cook, Haslewood, Hewett, Hieger, and Kennaway, *Proc. Roy. Soc.*, 1935, B, 117, 318). This suggested the desirability of examining for carcinogenic action other compounds containing the cholanthrene * ring system, and possible synthetic routes to this ring system have been under investigation in this Institute for the past year. We now describe a synthesis of the parent hydrocarbon, *cholanthrene*, by a method which establishes its structure. The same hydrocarbon has been obtained also by two other independent methods which will be described by two of us in a subsequent communication. The synthesis of methylcholanthrene, identical with that obtained from deoxycholic acid, has been announced recently by Fieser and Seligman (*J. Amer. Chem. Soc.*, 1935, 57, 228).

The starting point in our cholanthrene synthesis was the 1-iodoacenaphthene † of Morgan and Harrison (*J. Soc. Chem. Ind.*, 1930, 49, 413T). The Grignard compound of this iodoacenaphthene reacted with ethylene oxide to give β-1-*acenaphthylethyl alcohol*,

* For definition, see Wieland and Dane, *Z. physiol. Chem.*, 1933, 219, 241.

† We adhere to the convention commonly used in this Journal for the numbering of the acenaphthene ring. This differs from that used by Morgan and Harrison, who describe the compound in question as 2-iodoacenaphthene.

but the yield was extremely poor on account of the reluctance of the halogen compound to react with magnesium. No better result was obtained with 1-bromoacenaphthene. This difficulty was overcome, and the alcohol obtained in 55% yield, by making use of the recent device of Grignard (*Compt. rend.*, 1934, **198**, 625, 2217), who found that halogen compounds which are normally non-reactive towards magnesium readily give magnesio-derivatives in the presence of a molecule of ethyl bromide. β-1-*Acenaphthylethyl bromide* (I) condensed smoothly with the potassio-compound of ethyl *cyclo*hexanone-2-carboxylate, yielding *ethyl* 2-(β-1'-*acenaphthylethyl*)*cyclohexanone-2-carboxylate* (II), which was cyclised to *ethyl hexahydrocholanthrenecarboxylate* (III; R = Et) by boiling 55% sulphuric acid. An analogous synthesis of the chrysene ring system has been recorded by Ruzicka, Ehmann, Goldberg, and Hösli (*Helv. Chim. Acta*, 1933, **16**, 833). The ester (III; R = Et) was very difficult to hydrolyse, which accords with its structure; the corresponding *acid* (III; R = H) was obtained by heating with sodium ethoxide. This acid, when heated for an hour at 300° with platinum-black, gave *cholanthrene* (IV).
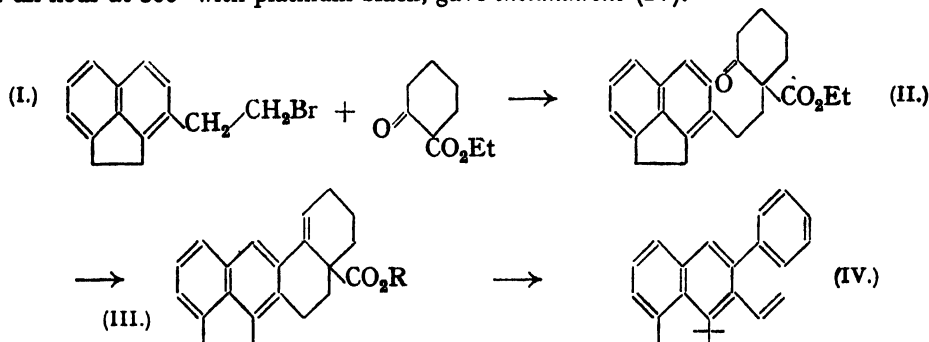
Additional evidence of the structure of the hydrocarbon so obtained was afforded by its oxidation by chromic acid to an acid which gave the Liebermann anthraquinol reaction. This acid, formed by fission of the five-membered ring at the point indicated by the dotted line, was decarboxylated to 5-methyl-1 : 2-benzanthraquinone, a degradation exactly comparable with the transformation of methylcholanthrene into 5 : 6-dimethyl-1 : 2-benzanthraquinone (Cook and Haslewood, *loc. cit.*).

Cyclisation of 2-*methyl*-(β-1'-*acenaphthylethyl*)-Δ^1-*cyclohexene* (V), obtained from β-1-acenaphthylethylmagnesium chloride and 2-methyl*cyclo*hexanone, by aluminium chloride led to an inseparable mixture of hydrocarbons, one of which appeared to be unaffected by treatment with selenium at 320°, a behaviour consistent with its formulation as the spiran (VI).
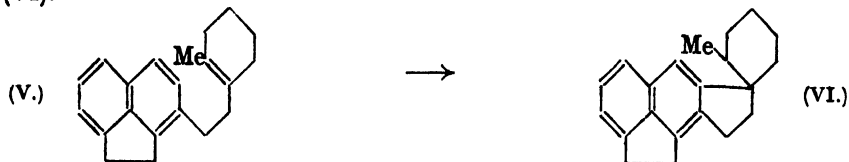
Hence this reaction was unsuitable for the synthesis of cholanthrene. In view of the favourable influence of a similarly disposed methyl group in promoting cyclisation of arylethyl*cyclo*pentenes to condensed-ring compounds, with avoidance of spiran formation (Cohen, Cook, Hewett, and Girard, J., 1934, 653; Cook, Hewett, Mayneord, and Roe, *ibid.*, p. 1727), the failure to obtain a satisfactory yield of octahydrocholanthrene by cyclisation of (V) was somewhat surprising. Consideration of stereochemical and other factors showed it to be unlikely that such an influence of a methyl group would depend upon the size of the ring to which this group is attached, but in order to examine this possibility the cyclisation of 2-*methyl*-(β-1'-*naphthylethyl*)-Δ^1-*cyclohexene* (VII) has been studied. Previous experiments had shown that the analogous hydrocarbon without the methyl group is converted by aluminium chloride into a mixture of saturated isomerides, the

principal constituent of which is 7 : 8-dihydrophenalyl-7-*spirocyclo*hexane, readily isolated by means of its sparingly soluble picrate (Cook and Hewett, J., 1934, 365). As was expected by analogy with the *cyclo*pentene derivatives already studied, this spiran formation was suppressed in the case of the methyl compound (VII) now reported, for the only cyclisation product which could be isolated was methyloctahydrochrysene (VIII).
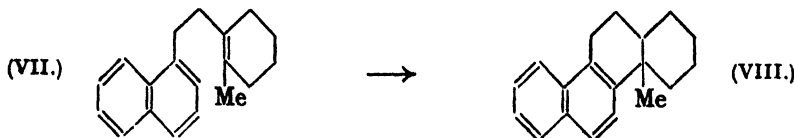
From this it is evident that the cyclisation of (V) is anomalous, but in the absence of further data we are unable to offer any explanation of the anomaly.

Methyloctahydrochrysene (VIII) was dehydrogenated to chrysene by selenium at 300°, but was unaffected by platinum-black. Failure of the latter catalyst to dehydrogenate hydroaromatic compounds containing quaternary carbon atoms was first observed by Zelinsky (*Ber.*, 1923, **56**, 1716). An example of a hydroaromatic compound which is dehydrogenated by platinum, but not by selenium, at 300°, will be given in a future communication (Cook and Hewett).

EXPERIMENTAL.

* and † denote microanalyses by Dr. A. Schoeller and Dr. G. Weiler respectively.

β-1-*Acenaphthylethyl Alcohol.*—The nitration of acenaphthene with diacetylorthonitric acid, the separation of the 1-nitro-compound and its reduction by aluminium amalgam, and the conversion of the amine into 1-iodoacenaphthene were carried out exactly as described by Morgan and Harrison (*loc. cit.*). Purification of the iodo-compound was best effected by vacuum distillation (b. p. 158°/0·3 mm.), followed by recrystallisation from alcohol.

Ethyl bromide (10·8 c.c.), diluted with anhydrous ether (100 c.c.), was gradually added to a mixture of 1-iodoacenaphthene (40 g.), magnesium turnings (7 g.), and anhydrous ether (100 c.c.). After all had been added and the reaction had subsided, the whole was boiled for 1¼ hours. The ice-cold solution was then slowly treated with ethylene oxide (25 g.) in ethereal solution, then kept at 0° for ½ hour, and finally at room temperature over-night. Toluene (50 c.c.) was added, the ether removed on the water-bath, and the residue heated at 100° for an hour. The product was treated with dilute hydrochloric acid, extracted with ether, dried, and distilled in a vacuum. β-1-*Acenaphthylethyl alcohol* (14·9 g., b. p. 179—180°/0·3 mm.) formed a pale yellow liquid which readily crystallised, and was purified for analysis through its 3 : 5-*dinitrobenzoate*, which crystallised from benzene–alcohol in microscopic yellow needles, m. p. 233—234·5° (Found : C, 64·2; H, 4·5. $C_{21}H_{16}O_6N_2$ requires C, 64·3; H, 4·1%). The alcohol obtained by hydrolysis of this ester crystallised from ligroin in colourless plates, m. p. 94—95° (Found : C, 85·0; H, 7·4. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%).

β-1-*Acenaphthylethyl chloride* (28·2 g.) was obtained from the alcohol (33·7 g.) by means of thionyl chloride and dimethylaniline (compare Cook and Hewett, J., 1933, 1107). This chloride (b. p. 145—150°/0·1 mm.) crystallised from alcohol in almost colourless rhombs, m. p. 54—55° (Found : Cl, 16·5. $C_{14}H_{13}Cl$ requires Cl, 16·4%).

β-1-*Acenaphthylethyl bromide* (I) was obtained by addition of phosphorus tribromide (10 g.) to a solution of the alcohol (20 g.) in carbon tetrachloride (28 c.c.) at 60°. After being kept at this temperature for ¼ hour, the solution was twice shaken with dilute aqueous sodium carbonate, and the filtered carbon tetrachloride solution distilled. The bromide, b. p. 165°/0·4 mm., crystallised from alcohol in rectangular plates (13 g.), m. p. 66° († Found : C, 64·2; H, 5·1. $C_{14}H_{13}Br$ requires C, 64·4; H, 5·0%).

Ethyl 2-(β-1'-*Acenaphthylethyl*)*cyclohexanone-2-carboxylate* (II).—Powdered potassium (3·3 g.) was dissolved in a mixture of ethyl *cyclo*hexanone-2-carboxylate (14·2 g.) and pure anhydrous benzene (50 c.c.), and the solution heated on the water-bath for 6 days with β-1-acenaphthylethyl bromide (11 g.). The whole was treated with ice and extracted with ether. The *keto-ester* (II) was isolated by distillation (10·6 g.; b. p. 210—220°/0·4 mm.), forming a colourless gum which slowly crystallised. After recrystallisation from alcohol it formed colourless stout needles (7 g.), m. p. 76—77° († Found : C, 79·2; H, 7·3. $C_{23}H_{26}O_3$ requires C, 78·8; H, 7·5%). Hydrolysis of this ester with methyl-alcoholic potash gave α-(β'-1-*acenaphthyl-ethyl*)*pimelic acid*, which was crystallised from benzene and then alcohol, forming colourless

rectangular plates, m. p. 165° († Found : C, 74·3; H, 7·1. $C_{21}H_{24}O_4$ requires C, 74·0; H, 7·1%).

Ethyl Hexahydrocholanthrenecarboxylate (III).—An attempt to effect cyclisation of the keto-ester (II) by boiling sulphuric acid (equal volumes of concentrated acid and water), a procedure successfully used in other cases (Ruzicka, *loc. cit.*; Cohen, Cook, and Hewett, this vol., p. 445), led only to amorphous black polymerisation products. When the concentration of sulphuric acid was 50% by weight, the keto-ester was recovered unchanged. However, a small increase in this concentration sufficed for cyclisation : A suspension of the keto-ester (II) (1·9 g.) in water (18·4 c.c.) and concentrated sulphuric acid (12 c.c.) was boiled for 30 hours. The product was isolated by ether extraction and distilled in a high vacuum from a bath at 200°. The pale yellow distillate was recrystallised several times from alcohol. *Ethyl hexahydrocholanthrenecarboxylate* (III; R = Et) (0·5 g.) formed long colourless needles, m. p. 150° (* Found : C, 82·8; H, 7·2; *M*, Rast method, 356, 365. $C_{22}H_{24}O_2$ requires C, 83·1; H, 7·3%; *M*, 332). Solutions of this ester had an intense violet fluorescence. For hydrolysis to *hexahydrocholanthrenecarboxylic acid* (III; R = H) the ester (0·45 g.) was heated at 180° for 18 hours with sodium ethoxide (2 g. of sodium in 30 c.c. of alcohol). A specimen of the precipitated acid crystallised from acetic acid in stout yellowish prisms, m. p. 241—242° with gas evolution (* Found : C, 82·0; H, 6·6. $C_{21}H_{20}O_2$ requires C, 82·85; H, 6·6%). The low value for carbon was probably due to absorption of oxygen during recrystallisation, during which the colourless solution became markedly yellow.

Cholanthrene (IV).—A mixture of the crude hexahydrocholanthrenecarboxylic acid (0·37 g.) and platinum-black (0·2 g.) was heated at 295—305° for 1¼ hours. The product was extracted with benzene, and the concentrated extract treated with alcohol. The crystalline product (0·2 g.) was sublimed at 170—190°/0·05 mm., and the sublimate recrystallised from benzene-alcohol. *Cholanthrene* (IV) formed pale yellow leaflets, m. p. 170—171° (* Found : C, 94·5, 94·3; H, 5·5, 5·6; *M*, Rast method, 255, 262. $C_{20}H_{14}$ requires C, 94·45; H, 5·55%; *M*, 254). The *picrate* crystallised from benzene in purplish-black needles, m. p. 167—168° (* Found : C, 64·5; H, 3·6. $C_{20}H_{14},C_6H_3O_7N_3$ requires C, 64·6; H, 3·55%). The m. p. of the hydrocarbon was unaltered by purification through the picrate.

Oxidation of cholanthrene (40 mg.) with sodium dichromate in acetic acid, and decarboxylation of the crude acid with boiling quinoline containing copper powder, was carried out as in the case of methylcholanthrene (Cook and Haslewood, *loc. cit.*). The resulting quinone, after vacuum sublimation and recrystallisation from acetic acid, had m. p. 166—168°, not depressed by 5-methyl-1 : 2-benzanthraquinone (m. p. 174°; Cook, J., 1933, 1596). There was insufficient for complete purification.

2-Methyl-(β-1'-acenaphthylethyl)-Δ¹-cyclohexene (V).—To an ice-cold Grignard solution prepared from β-1-acenaphthylethyl chloride (21·3 g.), anhydrous ether (150 c.c.), and magnesium turnings (2·5 g.) activated with iodine, was added 2-methyl*cyclo*hexanone (12·3 g.). After 16 hours at room temperature the product was treated with ice and dilute hydrochloric acid, and the ethereal solution washed and distilled. The fraction, b. p. 120—125°/0·4 mm., consisted of 1-*ethylacenaphthene*, which was purified through its *picrate*, bright red needles (from alcohol-*cyclo*hexane), m. p. 102—102·5° (Found : C, 58·2; H, 5·0. $C_{14}H_{14},C_6H_3O_7N_3$ requires C, 58·4; H, 4·2%). The hydrocarbon isolated from this picrate was distilled in a vacuum over sodium and then recrystallised from methyl alcohol, forming colourless needles, m. p. 30° (Found : C, 92·1; H, 7·8. $C_{14}H_{14}$ requires C, 92·2; H, 7·8%).

The higher-boiling fraction from the products of the Grignard reaction (11 g., b. p. 210°/0·7 mm.) formed a viscous liquid, which was heated for an hour at 155—165° with potassium hydrogen sulphate (16·5 g.), and then redistilled over sodium. Treatment with alcoholic picric acid gave the *picrate* of 2-*methyl-(β-1'-acenaphthylethyl)-Δ¹-cyclohexene*, golden-red needles, m. p. 107—108° (Found : C, 64·2; H, 5·8. $C_{21}H_{24},C_6H_3O_7N_3$ requires C, 64·1; H, 5·4%). The *hydrocarbon* (V), regenerated from this picrate and distilled over sodium, formed a pale yellow, viscous liquid, b. p. 182—185°/0·2—0·3 mm. (Found : C, 91·2; H, 8·5. $C_{21}H_{24}$ requires C, 91·2; H, 8·8%).

Cyclisation of 2-Methyl-(β-1'-acenaphthylethyl)-Δ¹-cyclohexene.—Anhydrous aluminium chloride (10·3 g.) was added to an ice-cold solution of the foregoing hydrocarbon (10·7 g.) in carbon disulphide (100 c.c.). After keeping at 0° for 21 hours, the dark green liquid was decanted from the aluminium chloride sludge and worked up in the usual way. The product, b. p. 200°/0·4 mm., was a yellow oil which crystallised on cooling. By repeated crystallisation from benzene, the m. p. of the bright red picrate obtained from the product was raised to 157—158°, and this gave, after removal of the picric acid, followed by four recrystallisations

from light petroleum, colourless needles, m. p. 178—182° (*Found : C, 90·9; H, 8·7%). We believe this to be mainly the spiran (VI), although evidence of this is lacking.

The hydrocarbon mixture (4 g.), m. p. 123—129°, from which this product had been separated was heated with selenium (4·6 g.) at 320—330° for 32 hours. After distillation and recrystallisation, the product had m. p. 120—125°. By crystallisation of the picrate from benzene, followed by removal of picric acid, the m. p. was brought to 165—173°, and was not depressed by the above product, m. p. 178—182°. Thus it appeared that the original cyclised material contained a constituent which resisted the dehydrogenating action of selenium. Whether cholanthrene was also present in the mixture after dehydrogenation we are unable to say, as no pure compound could be isolated from the amount of material available.

2-Methyl-1-(β-1'-naphthylethyl)cyclohexanol.—2-Methyl*cyclo*hexanone (31 g.) was added gradually to an ice-cold Grignard solution prepared from β-1-naphthylethyl chloride (48 g.), magnesium turnings (6 g.), and anhydrous ether (125 c.c.). Ice and ammonium chloride were added after 2 hours at room temperature, and the product was worked up in the usual way. The crude carbinol (36 g.) formed a thick syrup, b. p. 185—195°/0·5 mm., which could not be obtained crystalline. It was characterised by its 3 : 5-*dinitrobenzoate*, which crystallised from ligroin in pale yellow, hexagonal prisms, m. p. 136° († Found : C, 67·7; H, 5·8. $C_{26}H_{26}O_6N_2$ requires C, 67·5; H, 5·7%). During the purification of this compound there was also isolated a colourless crystalline neutral substance of lower carbon and hydrogen content († Found : C, 45·55; H, 2·8%), which was sparingly soluble in benzene but readily soluble in alcohol.

2-Methyl-(β-1'-naphthylethyl)-Δ¹-cyclohexene (VII).—This was obtained by dehydration of the foregoing carbinol (10 g.) with potassium hydrogen sulphate (10 g.) at 160—170° (1 hour). The distilled product (7 g.) was purified through its picrate, which readily dissociated and could not be obtained analytically pure. The regenerated *hydrocarbon* (VII), distilled over sodium, formed a colourless viscous liquid, b. p. 135°/0·1 mm., $d_4^{8°}$ 1·0158, $n_D^{8°}$ 1·5992, $[R_L]_D$ 83·1 (calc., 83·22) (Found : C, 90·9; H, 8·9. $C_{19}H_{22}$ requires C, 91·1; H, 8·9%).

Methyloctahydrochrysene (VIII).—Cyclisation of the unsaturated hydrocarbon (VII) (11 g.) with anhydrous aluminium chloride (13 g.) in carbon disulphide (100 c.c.) at 0° was complete in 7 hours. The distilled product (6·6 g.) was treated with alcoholic picric acid. After several recrystallisations from alcohol the *picrate* of *methyloctahydrochrysene* formed deep orange needles, m. p. 105—106° (* Found : C, 62·7; H, 4·7. $C_{19}H_{22},C_6H_3O_7N_3$ requires C, 62·6; H, 5·2%). No other crystalline product could be isolated from the liquors, although concentration gave a heavy oil, apparently a hydrocarbon which formed no picrate. It may be remarked that only one of the two stereoisomeric *as.*-octahydrochrysenes forms a picrate (Cook and Hewett, J., 1934, 373). *Methyloctahydrochrysene* (VIII), distilled over sodium, formed a thick colourless syrup, b. p. 145°/0·1 mm. (Found : C, 90·8; H, 9·0. $C_{19}H_{22}$ requires C, 91·1; H, 8·9%).

Dehydrogenation of methyloctahydrochrysene. (i) The pure hydrocarbon (0·5 g.) was heated with excess of selenium at 295—305° for 20 hours. The resulting chrysene, obtained in good yield, was identified by mixed m. p. with an authentic sample, and by conversion into its 2 : 7-dinitroanthraquinone complex. (ii) Methyloctahydrochrysene (1 g.) was heated with platinum-black (0·5 g.) at 300° for 8 hours. No crystals separated on cooling. After distillation the substance gave the picrate of the original methyloctahydrochrysene.

148. *The Mononitration of a-Naphthol and of a-Naphthyl Methyl Ether, and the Monoreduction of 2 : 4-Dinitro-a-naphthol.*

By HERBERT H. HODGSON and ERNEST W. SMITH.

PICTET and v. KRIJANOWSKI (*Chem. Zentr.*, 1903, II, 1109) state that the reaction between diacetylorthonitric acid and α-naphthol gives 2-nitro-1-naphthol and α-naphthaquinone, whereas in a table published by Bell (J., 1933, 286) the initial nitration of α-naphthol is recorded as occurring at position 4. Since α-naphthol under a variety of nitration con-

ditions, even including a deficiency of nitric acid, affords 2 : 4-dinitro-1-naphthol, we repeated the work of the former authors and obtained a 84% yield of 2-nitro-1-naphthol but no α-naphthaquinone. When α-naphthyl acetate was used instead of α-naphthol, the yield of 2-nitro-1-naphthol was 45%; the acetate, however, was very prone to dinitration.

Pictet and v. Krijanowski (*loc. cit.*) also state that the mononitration of α-naphthyl methyl ether gives 2-nitro-1-naphthyl methyl ether, whereas Bell's table records a mixture of the 2- and the 4-isomeride. Actually the bulk of the product is 4-nitro-1-naphthyl methyl ether, and the presence of the 2-nitro-compound has not been detected, a result to be anticipated from the electronic theory, since the inductive electron-attracting $(-I)$ effect of the methoxyl group would favour nitration in the more remote 4-position (compare also Ingold, *Ann. Reports*, 1928, **25**, 122; Hodgson and Clay, J., 1929, 2776).

Further nitration of both 2- and 4-nitro-1-naphthyl methyl ether gives almost entirely 2 : 4-dinitro-1-naphthyl methyl ether; no 4 : 5-dinitro-1-naphthyl methyl ether was detected (compare Bell's table).

2 : 4-Dinitro-1-naphthol is reduced almost quantitatively by stannous chloride in alcoholic hydrochloric acid to 2-*nitro-4-amino*-1-*naphthol*, but the composition of the mixture of nitroamines obtained by similar reduction of 2 : 4-dinitro-1-naphthyl methyl ether indicates an approach towards electropositive equality of the nitro-groups in this compound.

Diazotisation of 2-nitro-4-amino-1-naphthol under ordinary conditions gives a stable 2-*nitro-4-diazonaphthalene* 1-*oxide*, which couples with β-naphthol in acetic acid solution only on addition of hydrochloric acid.

Owing to salt formation, the aceto-4-halogeno-2-nitro-1-naphthalides are very resistant to hydrolysis by caustic alkalis. They are, however, gradually converted by boiling hydrochloric acid into the amines, which are readily transformed by boiling alkalis into the 4-halogeno-2-nitro-1-naphthols.

On halogenation, 2-nitro-4-amino-1-naphthol readily forms 3-halogeno-2-nitro-4-amino-1-naphthols, the homonuclear constitution being established by oxidation to phthalic anhydride, and by the synthesis of 3-*bromo-2-nitro-4-amino*-1-*naphthol* from authentic 2-bromo-4-nitro-1-naphthylamine (Hodgson and Elliott, J., 1934, 1706).

EXPERIMENTAL.

Nitration of α-Naphthol.—A solution of α-naphthol (5 g.) in acetic anhydride (20 c.c.) was treated gradually, below 7° during 1¼ hours, with diacetylorthonitric acid (7 c.c.) in acetic anhydride (10 c.c.). The dark mixture was poured on ice (see below), and the black precipitate (8 g.) repeatedly extracted with 2% aqueous sodium carbonate; the filtered extracts, on acidification, afforded only 2-nitro-1-naphthol (2·2 g.).

Nitration of α-Naphthyl Acetate.—The acetate (6·5 g.), treated exactly as above, gave a product free from blackening, which yielded 3·0 g. of 2-nitro-1-naphthol by the alkali extraction. When, however, the reaction mixture was kept for 3 hours, crystals appeared, which were identified as 2 : 4-dinitro-1-naphthol (m. p. 138°). Cautious addition of ice increased the precipitation to 2·5 g., but the mother-liquor when poured on ice gave much unchanged α-naphthyl acetate. Tetranitromethane did not react with α-naphthyl acetate either in methyl-alcoholic or in glacial acetic acid solution.

Nitration of α-Naphthyl Methyl Ether.—The ether (10 g.), dissolved in acetic anhydride (20 c.c.), was treated gradually at 3—5° during 3 hours with a solution of diacetylorthonitric acid (15 c.c.) in acetic anhydride (10 c.c.); the mixture was kept over-night, diluted with water (60 c.c.), and again kept over-night. The precipitate (12·5 g.), after two crystallisations from alcohol, formed long yellow needles, m. p. 85°, identical with authentic 4-nitro-1-naphthyl methyl ether (Found : N, 7·0. Calc. for $C_{11}H_9O_3N$: N, 6·9%); the m. p. was depressed by 2-nitro-1-naphthyl methyl ether (m. p. 80°. Cf. Clemo, Cockburn, and Spence, J., 1931, 1271).

Methylation of 4-Nitro-1-naphthol.—4-Nitro-1-naphthylamine (20 g.) was boiled (5 hours) with 10% aqueous sodium hydroxide (200 c.c.), and the cooled solution acidified to precipitate 4-nitro-1-naphthol. This naphthol (10 g.) was ground with potassium carbonate (10 g.), and the mixture heated (1 hour) on the water-bath with methyl sulphate (10 c.c.). After extrac-

tion with aqueous sodium carbonate, the insoluble 4-nitro-1-naphthyl methyl ether crystallised from alcohol as above, m. p. 85° (Found : N, 7·1%).

Reduction of 4-Nitro-1-naphthyl Methyl Ether.—The ether (8 g., obtained by either of the methods described above) was heated on the water-bath with 5·% aqueous acetic acid (100 c.c.), iron filings (10 g.) added gradually, and the heating continued for 2 hours. The liquid was filtered hot, cooled, and shaken with acetic anhydride (10 c.c.); 4-acetamido-1-naphthyl methyl ether, which separated, crystallised from alcohol in lustrous pearly-white needles, m. p. 187° (Woroshzow, *Chem. Zentr.*, 1911, I, 650, gives m. p. 180—181°) (Found : N, 6·7, 6·6. Calc. : N, 6·5%). This ether (1 g.), dissolved in acetic anhydride (2 c.c.), was nitrated with a mixture of diacetylorthonitric acid (1·5 c.c.) and acetic anhydride at 18—20°; 3-*nitro-4-acet-amido-1-naphthyl methyl ether*, which separated over-night, crystallised from alcohol in yellow needles, m. p. 246° (Found : N, 11·0. $C_{13}H_{12}O_4N_2$ requires N, 10·8%).

Nitration of 2- and 4-Nitro-1-naphthyl Methyl Ether.—Either compound (5 g.), suspended in acetic anhydride (20 c.c.), was treated gradually with diacetylorthonitric acid (10 c.c.), the temperature rising to *ca.* 70°. The product, twice crystallised from alcohol, gave cream-coloured needles of 2 : 4-dinitro-1-naphthyl methyl ether, m. p. 95° (Ullmann and Bruck, *Ber.*, 1908, **41**, 3938, describe yellow needles from methyl alcohol, m. p. 87°) (Found : N, 11·3, 11·4. Calc. : N, 11·3%). Demethylation with concentrated sulphuric acid gave 2 : 4-dinitro-1-naphthol.

Monoreduction of 2 : 4-Dinitro-1-naphthol.—The naphthol (5 g.), suspended in concentrated hydrochloric acid (20 c.c.) and alcohol (10 c.c.), was stirred for 1 hour during the addition below 30° of a solution of crystallised stannous chloride (15 g.) and alcohol (20 c.c.). After 12 hours, the *hydrochloride* of 2-*nitro-4-amino-1-naphthol* separated in pale yellow needles (5 g.; 98% yield), m. p. 175° (decomp.) after recrystallisation from alcoholic hydrochloric acid (Found : Cl, 14·6. $C_{10}H_8O_3N_2$,HCl requires Cl, 14·8%). Hydrolysis with water produced 2-nitro-4-amino-1-naphthol, which crystallised from alcohol in iridescent maroon needles, m. p. 160° (decomp.) (Found : N, 13·9. $C_{10}H_8O_3N_2$ requires N, 13·7%), gave an intensely red sodium salt, and was converted on deamination into 2-nitro-1-naphthol. 2-Nitro-4-acetamido-1-naphthol crystallised from glacial acetic acid in yellow-orange needles, m. p. 250° (decomp.) (Found : N, 11·6. Calc. : N, 11·4%) (Panizzon-Favre, *Gazzetta*, 1924, **54**, 826, gives m. p. 238°), and 2-*nitro-4-acetamido-1-naphthyl methyl ether* in stellate clusters of buff needles, m. p. 214° (Found : N, 10·9. $C_{13}H_{12}O_4N_2$ requires N, 10·8%). 2-*Nitro-4-benzamido-1-naphthol* crystallised from alcohol in orange needles, m. p. 230° (decomp.) (Found : N, 9·3. $C_{17}H_{12}O_4N_2$ requires N, 9·1%).

2-*Nitro-4-diazonaphthalene* 1-*oxide* was prepared by suspending the hydrochloride of 2-nitro-4-amino-1-naphthol (4·3 g.) in concentrated hydrochloric acid (30 c.c.; *d* 1·16) and water (30 c.c.), and adding 20% aqueous sodium nitrite with stirring until it was just in permanent excess. The diazo-oxide, collected after 12 hours, crystallised from alcohol or 80% acetic acid in pale yellow needles, m. p. 163° (decomp.) (Found : N, 19·8. $C_{10}H_5O_3N_3$ requires N, 19·5%). From it, by the Sandmeyer process, were prepared 4-*chloro-2-nitro-1-naphthol*, yellow needles from 70% alcohol, m. p. 155° (Found : Cl, 15·7. $C_{10}H_6O_3NCl$ requires Cl, 15·9%), 4-bromo-2-nitro-1-naphthol, yellow needles from 80% alcohol, m. p. 144° (Biedermann and Remmers, *Ber.*, 1874, **7**, 539, give m. p. 142°) (Found : Br, 29·7. Calc. : Br, 29·8%), and 4-iodo-2-nitro-1-naphthol, yellow needles from 80% alcohol, m. p. 152° (Meldola and Streat-feild, *J.*, 1895, **67**, 913, give m. p. 150°) (Found : I, 40·2. Calc. : I, 40·3%). In each case the compound reddens prior to fusion.

Other Reactions of 2-Nitro-4-diazonaphthalene 1-*Oxide.*—(a) Coupling with β-naphthol requires the presence of mineral acid ; 2-*nitro-1-hydroxynaphthalene-4-azo-β-naphthol* crystallised from glacial acetic acid in iridescent, deep red plates, m. p. 233° (decomp.) (Found : N, 11·9. $C_{20}H_{13}O_4N_3$ requires N, 11·7%), which gave a blue-violet colour with concentrated sulphuric acid, gradually changing through blue to green ; the sodium salt was deep red, almost black.

(b) Decomposition by potassium xanthate and hydrolysis of the resulting xanthate to a mercaptan, gave on oxidation by alkali ferricyanide, 3 : 3'-*dinitro-4* : 4'-*dihydroxydinaphthyl disulphide*, which crystallised from glacial acetic acid in pale yellow micro-needles, m. p. 197° (decomp.) (Found : S, 14·6. $C_{20}H_{12}O_6N_2S_2$ requires S, 14·5%).

(c) Decomposition by dilute sulphuric acid on the boiling water-bath gave mainly 2-nitro-1-naphthol.

Reactions of 2-Nitro-4-amino-1-naphthol.—(a) *Nitration.* The base (1 g.) was stirred with 10% aqueous nitric acid (20 c.c.) at room temperature until it dissolved. 2 : 3-*Dinitro-4-amino-1-naphthol*, collected after 12 hours, crystallised from 80% acetic acid in pale orange

needles, m. p. 130° (Found : N, 17·0. $C_{10}H_7O_5N_3$ requires N, 16·9%), and gave a red-orange potassium salt.

(b) *Chlorination.* The base in cold chloroform was treated with chlorine until the red colour disappeared; the *hydrochloride* of *3-chloro-2-nitro-4-amino-1-naphthol* separated in cream-coloured needles, which decomposed on heating (Found : Cl, 25·6. $C_{10}H_7O_3N_2Cl,HCl$ requires Cl, 25·8%); *3-chloro-2-nitro-4-amino-1-naphthol* crystallised from alcohol in yellow needles, m. p. 120° (Found : Cl, 14·8. $C_{10}H_7O_3N_2Cl$ requires Cl, 14·9%).

(c) *Bromination.* When the base (1 g.) in chloroform (30 c.c.) was stirred with bromine (0·5 c.c.) in chloroform (10 c.c.), *3-bromo-2-nitro-4-amino-1-naphthol* separated; it crystallised from alcohol in pale orange needles, m. p. 123° (Found : Br, 28·1. $C_{10}H_7O_3N_2Br$ requires Br, 28·3%). In dry chloroform, the unstable hydrobromide of the base separated, but was readily hydrolysed by atmospheric moisture. The constitution was established as follows : 2-bromo-4-nitro-1-naphthylamine (10·5 g.), suspended in 50% aqueous acetic acid (100 c.c.), was heated on the water-bath during the gradual addition (2 hours) of iron filings (10 g.). After dilution with hot water (100 c.c.), the liquid was filtered hot, cooled, and shaken with acetic anhydride. 2-*Bromo-4-acetamido-1-naphthylamine*, which separated, crystallised from water in colourless needles, m. p. 230° (Found : Br, 28·7. $C_{12}H_{11}ON_2Br$ requires Br, 28·7%), and on nitration in acetic acid solution gave 2-*bromo-3-nitro-4-acetamido-1-naphthylamine :* this crystallised from water in cream-coloured needles, m. p. 300° (Found : Br, 24·7. $C_{12}H_{10}O_3N_3Br$ requires Br, 24·7%), and when boiled with 10% aqueous sodium hydroxide gave 3-bromo-2-nitro-4-amino-1-naphthol.

(d) *Iodination.* The base (1 g.) in chloroform (30 c.c.) was shaken with iodine (1·5 g.) in chloroform (10 c.c.), either with or without mercuric oxide. An orange product, m. p. 195°, was precipitated; the filtrate, on concentration, deposited *3-iodo-2-nitro-4-amino-1-naphthol* in pale orange needles, m. p. 138° (Found : I, 38·3. $C_{10}H_7O_3N_2I$ requires I, 38·5%).

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149. *Studies on Hydrogen Cyanide. Part V. Reactions of Imino-formylcarbylamine.*

By LEONARD E. HINKEL, ERNEST E. AYLING, and JOHN H. BEYNON.

IMINOFORMYLCARBYLAMINE (bimolecular hydrogen cyanide) was first obtained by Nef (*Annalen*, 1895, **287**, 337), and its constitution finally established by Hinkel and Dunn (J., 1930, 1836). According to Nef, the compound is converted into ammonium formate by heating with water at 100° under pressure; actually, hydrolysis occurs when the compound is dissolved in cold water, for ammonium formate is obtained on evaporation in a desiccator. This ready hydrolysis accounts for the discrepancy between the calculated and the actual analytical values for the compound described by Nef (*loc. cit.*) as the silver derivative of the hydrate of bimolecular hydrogen cyanide, C_2N_2HAg,H_2O, containing about 5% of adsorbed nitric acid. Nef prepared the derivative by mixing aqueous solutions of silver nitrate and bimolecular hydrogen cyanide, but no pure compound can be obtained in this way; the precipitates always contain nitrate in varying quantities and the composition varies with the concentration of the reactants and with the duration of time prior to filtration.

Iminoformylcarbylamine dissolves unchanged in absolute alcohol, and the addition of alcoholic silver nitrate, with either reactant in excess, leads to the formation of a white crystalline solid of constant composition, $2AgNO_3,5HCN$. This *compound* is slowly hydrolysed by cold water, in which it is slightly soluble, and explodes when heated.
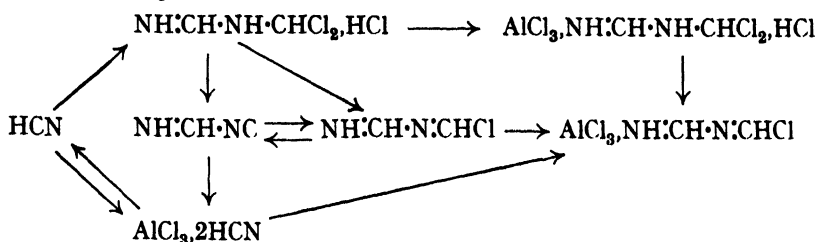
Iminoformylcarbylamine in ethereal solution also forms with mercuric chloride a *compound* which, by analysis, corresponds to $HgCl_2,3HCN$ or more probably $2HgCl_2, 3(HCN)_2$, since, with hydrogen chloride, it yields a deliquescent solid which appears to be the *compound* $2HgCl_2,3(2HCN,HCl)$. The latter reaction corresponds to the conversion of iminoformyl-carbylamine, $NH{:}CH{\cdot}NC$, by means of hydrogen chloride into chloromethyleneformamid-

ine, NH:CH·N:CHCl, as observed by Hinkel and Dunn (*loc. cit.*) instead of the formation of the sesquichloride as stated by Nef (*loc. cit.*).

Hydrogen cyanide unites with aluminium chloride to form the double compound $AlCl_3,2HCN$ (Hinkel and Dunn, J., 1931, 3243; compare Perrier, *Comp. rend.*, 1895, **120**, 1424). In a similar manner, iminoformylcarbylamine yields a double compound, $AlCl_3,(HCN)_2$, and this is identical with the compound obtained by Hinkel and Dunn from hydrogen cyanide. It melts at 125° with decomposition into hydrogen cyanide and aluminium chloride and although prepared from iminoformylcarbylamine, the latter could not be regenerated from it. The decomposition also occurs at 100° but at a much slower rate. The double compound does not combine with hydrogen chloride at the ordinary temperature, but at 80° reaction occurs, again with only one molecule of hydrogen chloride (compare above), yielding the *compound* $AlCl_3,NH:CH·N:CHCl$, identical with that obtained by the direct union of aluminium chloride and chloromethyleneformamidine. This double compound yields *p*-tolualdehyde when heated with toluene in the presence of free aluminium chloride.

The sesquichloride of hydrogen cyanide (dichloromethylformamidine hydrochloride) also yields a *double compound*, $AlCl_3,NH:CH·NH·CHCl_2,HCl$, and this readily decomposes into $AlCl_3,NH:CH·N:CHCl$ on heating. The decomposition also proceeds slowly in toluene at 100°, leading to the formation of a mixture of *p*-tolualdehyde and tolylhydrylformamidine hydrochloride. These two compounds result from the reaction on toluene of $AlCl_3,NH:CH·N:CHCl$ and $AlCl_3,NH:CH·NH·CHCl_2,HCl$ respectively (compare above and Gattermann and Schnitzpahn, *Ber.*, 1898, **31**, 1770).

The inter-relationship between hydrogen cyanide, iminoformylcarbylamine, and its hydrogen chloride derivatives and the double compounds with aluminium chloride is shown in the following scheme :

$$NH:CH·NH·CHCl_2,HCl \longrightarrow AlCl_3,NH:CH·NH·CHCl_2,HCl$$

$$HCN \quad NH:CH·NC \rightleftarrows NH:CH·N:CHCl \longrightarrow AlCl_3,NH:CH·N:CHCl$$

$$AlCl_3,2HCN$$

With aromatic primary amines, the sesquichloride of hydrogen cyanide and chloromethyleneformamidine both yield *NN'*-diarylformamidines (Dains, *Ber.*, 1902, **35**, 2496; Hinkel and Dunn, J., 1930, 1836) and the first stage in each of these reactions may consist in the removal of hydrogen chloride by the base with the formation of iminoformylcarbylamine (I), which then reacts with the base to give the diarylformamidine (II).

$$\underset{(I.)}{NH:CH·NC} \xrightarrow{R·NH_2} NH:CH·N=\!\!=CH·NHR \xrightarrow{R·NH_2} \underset{(II.)}{NH:CH·NH_2 + RN:CH·NHR}$$
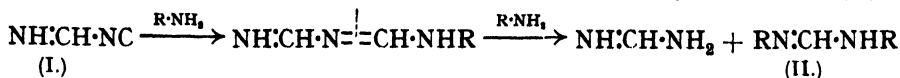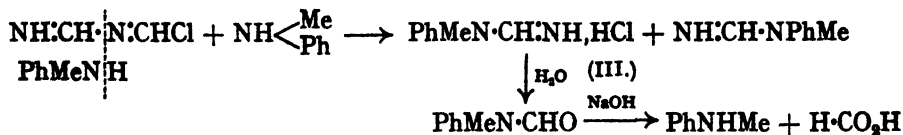
In support of this view, iminoformylcarbylamine has been found to react with primary amines to yield the diarylformamidines.

Dimethylaniline reacts with the two hydrogen chloride derivatives of iminoformylcarbylamine (Gattermann and Schnitzpahn, *loc. cit.*; Hinkel and Dunn, *loc. cit.*) but not with iminoformylcarbylamine itself. The initial stage in the formation of crystal-violet leuco-base with the hydrogen chloride derivatives must be, therefore, not complete removal of hydrogen chloride as with primary amines, but elimination of the chlorine atom attached to the NC group with the *p*-hydrogen of the dimethylaniline.

In order to complete the sequence of the study of the behaviour of aromatic amines with these compounds, the reactions with the comparable secondary amine, monomethylaniline, have now been examined. Since there is only one amine hydrogen atom, a different type of reaction must occur. Iminoformylcarbylamine does not react with monomethylaniline, but chloromethyleneformamidine and the sesquichloride of hydrogen cyanide both

yield N-*phenyl*-N-*methylformamidine hydrochloride* (III) when heated with the amine, indicating that the presence of the chlorine atom is necessary for the reaction, as in the case of dimethylaniline. The phenylmethylformamidine hydrochloride yields on hydrolysis, first, formylmethylaniline and, finally, monomethylaniline, a sequence similar to that obtained with benzhydrylformamidine hydrochloride by Gattermann and Schnitzpahn (*loc. cit.*).

$$NH{:}CH{\cdot}N{:}CHCl + NH{\Big<}{\begin{matrix}Me\\Ph\end{matrix}} \longrightarrow PhMeN{\cdot}CH{:}NH,HCl + NH{:}CH{\cdot}NPhMe$$

$$PhMeN{:}H \qquad\qquad\qquad\qquad \Big\downarrow {\scriptstyle H_2O} \quad (III.)$$

$$PhMeN{\cdot}CHO \xrightarrow{\ NaOH\ } PhNHMe + H{\cdot}CO_2H$$

When hydrogen chloride is passed into a solution of iminoformylcarbylamine in alcohol, formamidine hydrochloride and ethyl orthoformate result : chloromethyleneformamidine is probably first produced, since this compound with alcohol also gives rise to the same products. This action is similar to that of the sesquichloride of hydrogen cyanide with alcohol (Claisen and Matthews, *Ber.*, 1883, **16**, 309) in which, in addition to the formamidine hydrochloride and ethyl orthoformate, some ethyl chloride is formed. These compounds can only result from the ready decomposition of the sesquichloride into chloromethyleneformamidine and hydrogen chloride.

<center>EXPERIMENTAL.</center>

Preparation of Iminoformylcarbylamine.—Owing to the vigour of the reaction between quinoline and the sesquichloride of hydrogen cyanide, the iminoformylcarbylamine prepared by Hinkel and Dunn's method (J., 1930, 1838) nearly always contains traces of quinoline and its hydrochloride. It was readily obtained pure by the following procedure. The reaction flask was attached to a horizontal steam-jacketed tube, which in turn was connected to a similar water-cooled tube, followed by a U-tube immersed in solid carbon dioxide and alcohol. The quinoline was slowly run into the flask containing the sesquichloride and, after the vigorous reaction had subsided, warm dry air was slowly drawn through the apparatus. The impurities condensed in the steam-jacketed tube, and pure iminoformylcarbylamine, m. p. 85°, condensed as prismatic crystals in the water-cooled tube. The strongly cooled U-tube served to collect the small quantity of iminoformylcarbylamine not previously condensed and the free hydrogen cyanide which is always formed in the reaction.

For the preparation of small quantities of the carbylamine (5 g.), the requisite amount of sodium cinnamate may conveniently be substituted for the quinoline. With either chloromethyleneformamidine or the sesquichloride, the pure carbylamine was thus obtained in over 80% yield.

Hydrolysis.—Iminoformylcarbylamine was dissolved in water, and the resulting acid solution shaken with ether. The latter yielded no original substance on evaporation in a vacuum. The aqueous solution was evaporated to dryness in a vacuum over sulphuric acid and after 48 hours a white crystalline solid was obtained, consisting of pure ammonium formate, m. p. and mixed m. p. 114° (Yield, 0·68 g. from 0·31 g.; 94%).

Chloromethyleneformamidine.—This was prepared by Hinkel and Dunn's method (*loc. cit.*), with the exception that the sesquichloride was mixed with powdered aluminium (3 atoms); after prolonged heating at 100° in a vacuum, aluminium alone remained.

Action of Silver Nitrate on Iminoformylcarbylamine.—(1) *In aqueous solution.* Silver nitrate (1·7 g.; 1 mol.) in ice-water (100 c.c.) was added to iminoformylcarbylamine (1·08 g.; 2 mols.) in ice-water (20 c.c.). The white crystalline deposit was quickly removed, washed with ice-water and then with ether, and dried in a vacuum over sulphuric acid [Found : Ag, 53·75; N (alkaline hydrolysis), 12·7; N as NO_3 (alkaline reduction, Devarda's alloy), 3·0. C_2HN_3Ag,H_2O requires Ag, 60·3; N, 15·6%] (Nef, *loc. cit.*, records Ag, 54·5; N, 16·5%).

If the precipitated silver salt was kept in contact with the solution for an hour or more before filtration, the silver and the nitrogen content both diminished. In all cases the crystalline solids obtained were somewhat soluble in water, contained nitrate, exploded when heated, and darkened on exposure to light, especially when moist.

(2) *In alcoholic solution.* Solutions of silver nitrate (1 mol.) and iminoformylcarbylamine (2 mols.) in absolute alcohol were mixed. The resulting precipitate was washed three times

with alcohol and dried in a vacuum over sulphuric acid. The white crystalline solid, which contained nitrate and gave the characteristic reaction with a solution of diphenylamine in sulphuric acid, could be kept unchanged in light, but rapidly darkened in contact with moisture [Found : Ag, 44·8; N (alkaline hydrolysis), 14·5; N as NO_3 (alkaline reduction, Devarda's alloy), 6·0. $2AgNO_3,5HCN$ requires Ag, 45·4; N, 14·8; N as NO_3, 5·9%].

Action of Mercuric Chloride on Iminoformylcarbylamine.—Addition of mercuric chloride (4 g.; 1·5 mols.) in pure dry ether (250 c.c.) to iminoformylcarbylamine (0·54 g.; 1 mol.) in pure dry ether (50 c.c.) yielded a white crystalline solid (1·24 g.), which was washed with dry ether and dried in a vacuum over sulphuric acid (Found : Hg, 56·6; N, 11·7; Cl, 19·4. $HgCl_2,3HCN$ requires Hg, 56·8; N, 11·9; Cl, 20·1%). A repetition of the experiment, but with an excess of iminoformylcarbylamine ($[HCN]_2$, 0·95 g., 2 mols.; $HgCl_2$, 2·44 g., 1 mol.), yielded the same compound (1·8 g.) (Found : Hg, 56·7; N, 11·8; Cl, 19·7%). The compound is somewhat soluble in dry ether and in dry benzene and very soluble in cold water.

Action of Hydrogen Chloride on the Compound $HgCl_2,3HCN$.—A solution of the compound (2 g.) in dry ether (300 c.c.) was saturated with dry hydrogen chloride. Owing to the extremely deliquescent nature of the white solid deposited, its removal, the washing with dry ether, drying, and transference to a weighing bottle for analysis were performed in a specially designed box [Found : Hg, 48·0; N, 10·0; Cl, 30·0. $2HgCl_2,3(2HCN,HCl)$ requires Hg, 49·2; N, 10·3; Cl, 30·5%].

Action of Aluminium Chloride on Iminoformylcarbylamine.—Powdered aluminium chloride (3·3 g.; 1 mol.), mixed with iminoformylcarbylamine (1·7 g.; 1·25 mols.), was heated to 85°. Liquefaction first occurred and the liquid then rapidly solidified. The solid was rapidly crushed and placed in a vacuum desiccator to remove excess of the volatile iminoformylcarbylamine. The white solid obtained had m. p. 125°, unchanged by admixture with the compound $AlCl_3,2HCN$ prepared from aluminium chloride and hydrogen cyanide (Found : Cl, 56·2; N, 14·3. Calc. for $AlCl_3,2HCN$: Cl, 56·8; N, 14·5%).

The compound was heated at 100° for 3 hours under a water-cooled condenser attached to a U-tube immersed in solid carbon dioxide and alcohol. Hydrogen cyanide condensed as a solid in the U-tube, but no iminoformylcarbylamine was detected. A similar result was obtained when the compound was heated with quinoline.

Action of Aluminium Chloride on Chloromethyleneformamidine.—When powdered aluminium chloride (7 g.; 1·16 mols.) was added to chloromethyleneformamidine (4 g.; 1 mol.), the mixture partly liquefied with evolution of heat. The liquid was decanted from unchanged aluminium chloride and allowed to cool in the absence of moisture; it then yielded a white solid, m. p. 80° (Found : Cl, 62·9; N, 12·3. $AlCl_3,2HCN,HCl$ requires Cl, 63·4; N, 12·5%).

The compound $AlCl_3,2HCN,HCl$ was maintained at 100° for 2 hours in a flask attached to a horizontal air condenser fitted with a calcium chloride tube. Chloromethyleneformamidine condensed as a volatile and very deliquescent solid in the cooler parts of the condenser and was identified by analysis and by its reaction with toluene and aluminium chloride to yield *p*-tolualdehyde (see below).

Reaction of the Compound $AlCl_3,2HCN,HCl$ *with Toluene.*—The compound (3·7 g.; 1 mol.), suspended in dry toluene (30 c.c.), was heated with aluminium chloride (2·3 g.; 1 mol.) for 1 hour on a steam-bath. The red liquid obtained was poured on ice and concentrated hydrochloric acid and distilled with steam. Phenylhydrazine (5 c.c.) was added to the distillate, which was again distilled with steam to remove toluene and the excess of phenylhydrazine, leaving *p*-tolualdehydephenylhydrazone as a yellow solid, m. p. and mixed m. p. 114° (3·2 g.; 91%, calculated on the basis that $AlCl_3,2HCN,HCl$ yields 1 mol. of aldehyde).

Action of Hydrogen Chloride on $AlCl_3,2HCN$.—Hydrogen chloride was passed over the compound (5 g., prepared from hydrogen cyanide) in a U-tube. Reaction began at 80°, the solid gradually liquefying. The passage of hydrogen chloride was then discontinued, and the contents of the tube were protected from moisture while the temperature of the bath was raised to 100°. The compound gradually dissociated and after 2 hours chloromethyleneformamidine collected on the cooler parts of the tube and was identified by the addition of toluene (30 c.c.) and aluminium chloride (3·5 g.; 1 mol.) and proceeding as described above, *p*-tolualdehydephenylhydrazone being obtained (2·8 g.; 50%, calc. on the above basis).

Action of Aluminium Chloride on the Sesquichloride of Hydrogen Cyanide.—A mixture of aluminium chloride (13·3 g.; 1 mol.) and the sesquichloride (16 g.; 1 mol.), protected from moisture, liquefied when warmed to 65°, and set to a colourless crystalline solid, m. p. 62°, on cooling (Found : Cl, 71·6; N, 9·5. $AlCl_3,2HCN,3HCl$ requires Cl, 71·7; N, 9·4%).

Excess of aluminium chloride (8 g.; 1·2 mols.), added similarly to powdered sesqui-

chloride (8·1 g.; 1 mol.), yielded a liquid together with some unchanged aluminium chloride. Decantation and cooling of the liquid again yielded the above compound, m. p. 62°.

Reaction of the Compound AlCl₃,2HCN,3HCl *with Toluene.*—The compound (37 g.; 1 mol.) in dry toluene (50 c.c.) was heated under reflux at 70° for 1 hour and at 100° for 2 hours, the evolution of hydrogen chloride then having ceased. The mixture was poured on ice and concentrated hydrochloric acid and steam-distilled. The *p*-tolualdehyde present in the distillate was determined as its phenylhydrazone by the procedure described above. In order to determine the tolylhydrylamine, the residue remaining after the initial steam distillation in acid solution was basified and again steam-distilled, the tolylhydrylamine, m. p. 92° (acetyl derivative, m. p. 157°; compare Gattermann and Schnitzpahn, *loc. cit.*), being isolated from the distillate by extraction with ether (Yields : *p*-tolualdehydephenylhydrazone, 3·6 g., 14%; tolylhydrylamine, 3·6 g., 14%).

Reaction of the Compound AlCl₃,2HCN,3HCl *with Toluene in Presence of Aluminium Chloride.*— A mixture of the compound (37 g.; 1 mol.), dry toluene (43 c.c.), and aluminium chloride (17 g.; 1 mol.) was maintained under reflux at 50—55° for 3 hours; hydrogen chloride evolution being then complete, the reaction mixture was treated as described above. No phenylhydrazone was obtained from the first distillate, and the residue yielded tolylhydrylamine (22 g.; 84%).

Reaction of Iminoformylcarbylamine with Primary Aromatic Amines.—Solutions of iminoformylcarbylamine (1 mol.) and of the aromatic amine (2 mols.) in dry benzene were heated under reflux on the water-bath for a short time until the evolution of ammonia was complete and, after removal of the benzene, the solid product was purified by crystallisation. The product obtained with each amine was identical with that described by Dains (*loc. cit.*) and the yield was almost quantitative. Aniline, *p*-toluidine, *p*-bromoaniline, *p*-chloroaniline, *p*-anisidine, α- and β-naphthylamines readily yielded condensation products, but no condensation occurred with *o*- and *p*-nitroanilines, *m*-nitro-*p*-toluidine, or *p*-aminophenol (compare *idem, ibid.*).

Action of Monomethylaniline on Chloromethyleneformamidine.—Monomethylaniline (5 c.c.; 3 mols., *i.e.*, 1 mol. excess) and chloromethyleneformamidine (1·3 g.; 1 mol.) were mixed and heated at 100° for 5 minutes. The latter substance dissolved and the solution rapidly deposited a mass of fine, white, needle-shaped crystals, which were washed with dry ether, yielding *phenylmethylformamidine hydrochloride*, m. p. 192° (Found : Cl, 20·9; N, 16·3. C₈H₁₁N₃Cl requires Cl, 20·8; N, 16·4%) (2·1 g.; 86%). Attempted crystallisation from alcohol or aqueous alcohol led to partial decomposition of the compound.

Action of Water on Phenylmethylformamidine Hydrochloride.—The hydrochloride (5 g.), when boiled with water (30 c.c.), yielded an oil, which was extracted with ether. The dried extract yielded, on fractionation, formomethylanilide as a light brown oil, m. p. 8—10°, b. p. 244—245° (Pinner, *Ber.*, 1883, **16**, 1652, records b. p. 243—244°) (Found : N, 10·3. Calc. : N, 10·4%) (2 g.; 50%).

Action of Sodium Hydroxide Solution on Phenylmethylformamidine Hydrochloride.—The hydrochloride (1 g.), on boiling with 4*N*-sodium hydroxide for 5 minutes, yielded monomethylaniline (0·5 g.), which was extracted in ether and identified as its hydrochloride, m. p. and mixed m. p. 121°.

Action of Monomethylaniline on the Sesquichloride.—Monomethylaniline (7 c.c.; excess over 3 mols.) was slowly added to the sesquichloride (3 g.; 1 mol.); a vigorous action ensued, and the mixture was then heated at 100° for 10 minutes. The solid product, warmed with 4*N*-hydrochloric acid, yielded formomethylanilide (4 g.), b. p. 243—245°, which was extracted with ether (Found : N, 10·3. Calc. : N, 10·4%).

Reaction of Chloromethyleneformamidine with Ethyl Alcohol.—Ethyl alcohol, distilled from sodium (26 c.c.; 4 mols.) was added to chloromethyleneformamidine (10 g.; 1 mol.), protected from moisture. On cooling by immersion in cold water for 20 hours with occasional shaking, the solid gradually dissolved, finally yielding a viscous liquid and ammonium chloride (0·6 g.) (Found : N, 26·0. Calc. : N, 26·2%). The liquid, on fractionation, yielded ethyl orthoformate, b. p. 144—145° (9·9 g.; 60·5%), and an oily residue of formamidine hydrochloride, which solidified on cooling and crystallised from alcohol in long colourless needles (8·5 g.), m. p. 81° (Found : N, 34·7. Calc. : N, 34·8%).

A repetition of the above procedure, with subsequent heating under reflux on a steam-bath for 1 hour, yielded similarly ammonium chloride (1 g.), ethyl orthoformate (10 g.; 61%), and formamidine hydrochloride (8 g.; 89%).

The reactants in molecular proportion were kept at room temperature for 20 hours and heated at 100° for 1 hour, and unchanged chloromethyleneformamidine was removed by filtra-

tion of the hot liquid, which, on cooling, deposited formamidine hydrochloride (25%) and yielded, on fractionation, ethyl orthoformate (27%).

Action of Hydrogen Chloride on Iminoformylcarbylamine in Alcoholic Solution—Dry hydrogen chloride was passed into a solution of iminoformylcarbylamine (2·16 g.; 1 mol.) in alcohol, distilled from sodium (7·4 g.; 4 mols.), protected from moisture, for 2 hours at 0°. The resulting solution was kept at room temperature for 12 hours and heated under reflux on a steambath for 1 hour. By the procedure described above, formamidine hydrochloride (2·5 g.; 80%) and ethyl orthoformate (4 g.; 68%) were isolated.

The authors thank Imperial Chemical Industries, Ltd., for a grant and for gifts of aluminium chloride.

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150. *The Constitution and Reactions of Thiocarbonyl Tetrachloride. Part II. Reaction with Primary Arylamines, Phenols, and Reducing Agents.*
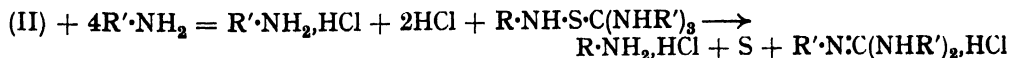
By JOSEPH M. CONNOLLY and G. MALCOLM DYSON.

HYDROLYSIS of the compound obtained by interaction of *p*-toluidine and thiocarbonyl tetrachloride (Connolly and Dyson, J., 1934, 822) gave *p*-tolylcarbylamine and *p*-tolylthiocarbimide; if isomeric change be precluded, this is evidence for an R–N–C– link in the original compound. Experiments hereinafter described show that this link is probably due to intermediate ring formation (III) during hydrolysis, since the substance for which
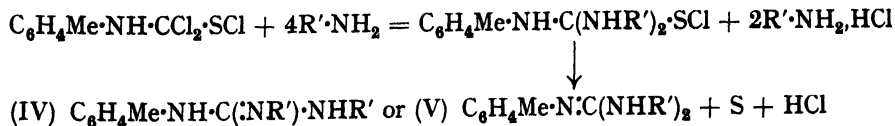
$$R \cdot NH \cdot CCl_2 \cdot SCl \qquad R \cdot NH \cdot S \cdot CCl_3 \longrightarrow R \cdot N \underset{CCl_2}{\overset{S}{\diagdown}} \longrightarrow \overset{R \cdot NC}{\underset{R \cdot NCS}{+}}$$

(I.) (II.) (III.)
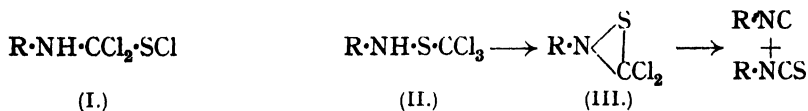
structure (I) had been suggested (*p*-toluidinodichloromethylchlorothiol) (I; R = C_6H_4Me) has been shown to be *S-p*-toluidinotrichloromethylthiol (II; R = C_6H_4Me).

In inert solvents (II) reacts with an arylamine (4 mols.), giving the tri-s-arylamino-derivative, each aryl group being derived from the amine taken:

$$(II) + 4R' \cdot NH_2 = R' \cdot NH_2, HCl + 2HCl + R \cdot NH \cdot S \cdot C(NHR')_3 \longrightarrow$$
$$R \cdot NH_2, HCl + S + R' \cdot N \vdots C(NHR')_2, HCl$$

Had the original compound been *p*-toluidinodichloromethylchlorothiol (I), a *p*-tolyl-diarylguanidine would have been obtained:
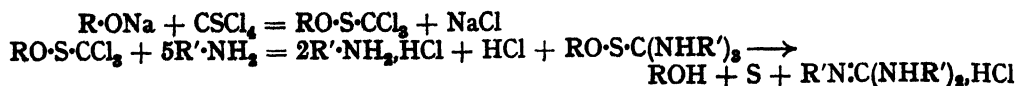
$$C_6H_4Me \cdot NH \cdot CCl_2 \cdot SCl + 4R' \cdot NH_2 = C_6H_4Me \cdot NH \cdot C(NHR')_2 \cdot SCl + 2R' \cdot NH_2, HCl$$
$$\downarrow$$

(IV) $C_6H_4Me \cdot NH \cdot C(\vdots NR') \cdot NHR'$ or (V) $C_6H_4Me \cdot N \vdots C(NHR')_2 + S + HCl$

No compound of the type (IV) or (V) was detected, triarylguanidines of the type $R' \cdot N \vdots C(NHR')_2$ only being obtained. The hydrochlorides of the latter are obtained pure and in good yield when the amine used contains the same aryl group as does the *S*-arylaminotrichloromethylthiol: this is a new and simple method of synthesising such triarylguanidines.

The action of thiocarbonyl tetrachloride on phenols is analogous to that on primary arylamines, *S-aryloxytrichloromethylthiols* being obtained. These are colourless or pale yellow oils, which decompose readily and in several cases cannot be distilled unchanged in a vacuum. They are slowly hydrolysed by boiling water, more readily by boiling 20% aqueous alkali, to the corresponding phenol. With hydrogen chloride in ether they regenerate thiocarbonyl tetrachloride and the phenol; reduction with zinc dust gives

methylthiol, and excess of arylamine in an inert solvent gives triarylguanidine hydrochlorides :

$$R \cdot ONa + CSCl_4 = RO \cdot S \cdot CCl_3 + NaCl$$
$$RO \cdot S \cdot CCl_3 + 5R' \cdot NH_2 = 2R' \cdot NH_2, HCl + HCl + RO \cdot S \cdot C(NHR')_2 \longrightarrow$$
$$ROH + S + R'N \vdots C(NHR')_2, HCl$$

Concentrated aqueous sodium thiosulphate converts thiocarbonyl tetrachloride into carbon disulphide and a trace of thiocarbonyl chloride. Gugliamelli, Novelli, Ruiz, and Anaslasi (*Anal. Asoc. Quím. Argentina*, 1927, **15**, 337) showed that thiocarbonyl chloride could be obtained from thiocarbonyl tetrachloride by reduction with stannous chloride in place of the more usual tin and hydrochloric acid (Dyson, " Organic Syntheses," VI, 86). A modification of this method using tetrachloroethane has resulted in a rapid and convenient method for the preparation of thiocarbonyl chloride in 65% yield. In a simple new method for preparing arylthiocarbimides in good yield without isolation of thiocarbonyl chloride, an arylamine is dissolved in hydrochloric acid containing stannous chloride and stirred with thiocarbonyl tetrachloride, the arylthiocarbimide being then removed either by filtration or by distillation in steam.

EXPERIMENTAL.

Triphenylguanidine.—S-Anilinotrichloromethylthiol (26 g.) was prepared by the method previously described (Connolly and Dyson, *loc. cit.*), ligroin (150 ml.) replacing ether as solvent. The ligroin solution, separated from the aqueous layer, was added to aniline (45 g.) in ligroin (100 ml.), and the whole boiled for a few minutes and kept for 48 hours with occasional shaking. Sulphur, aniline hydrochloride, and triphenylguanidine hydrochloride were filtered off, dried, and extracted with boiling water, followed by boiling dilute hydrochloric acid. Triphenylguanidine hydrochloride, which separated from the cooled extracts, was filtered off, and converted by a slight excess of warm dilute caustic soda solution into the base, which formed colourless needles (24 g.) from alcohol, m. p. 143°; picrate, deep yellow needles m. p. 179°.

Tri-p-tolylguanidine.—This was prepared : (*a*) From S-*p*-toluidinotrichloromethylthiol and *p*-toluidine by the method just described for the phenyl analogue; it formed white needles from alcohol, m. p. 122°. (*b*) From the same reactants with alcohol as solvent, from which crystalline sulphur, m. p. 119°, separated on cooling. (*c*) From S-anilinotrichloromethylthiol (13 g.) and *p*-toluidine (24 g.) in ligroin (250 ml.); after the mixture had been boiled for a few minutes and kept for 48 hours, tri-*p*-tolylguanidine was isolated as described above; a little triphenylguanidine was formed also, from aniline liberated during the reaction, and four recrystallisations were necessary completely to purify the *p*-tolyl compound, which then had m. p. 120·5°; mixed with authentic tri-*p*-tolylguanidine (m. p. 122°), it melted at 121°.

Phenyldi-p-tolylguanidine.—Phenylthiocarbimide (30 g.) in chloroform (90 ml.) was treated with chlorine until the increase in weight was 25 g. On distillation *iso*cyanophenyl dichloride passed over as a colourless oil between 206° and 212°; on redistillation it had b. p. 209°. The dichloride (4 g.) and *p*-toluidine (9·5 g.) in benzene (150 ml.) were boiled under reflux for 16 hours. The solid obtained was washed with cold water to remove *p*-toluidine hydrochloride, and the residual phenyldi-*p*-tolylguanidine hydrochloride converted by dilute caustic alkali solution into the base, which formed white needles from alcohol, m. p. 100°.

as-*Phenyldi-p-tolylguanidine*, $C_6H_4Me \cdot N \vdots C(NHPh) \cdot NH \cdot C_6H_4Me$.—Di-*p*-tolylthiourea (20 g.) in benzene (350 ml.) at 40° was stirred with mercuric oxide (18 g.) for ¼ hour, the filtered liquid allowed to evaporate after 2 hours, and monomeric di-*p*-tolylcarbodi-imide extracted from the residue by ether as a thick oil (11 g.). Di-*p*-tolylcarbodi-imide (7 g.) and aniline (4 g.) in benzene (40 ml.) were boiled for 12 hours, the benzene removed by evaporation, and the oily residue boiled with concentrated hydrochloric acid (25 ml.) and extracted with boiling water. The cooled extract deposited crystals of as-phenyldi-*p*-tolylguanidine hydrochloride; the base formed small colourless needles from alcohol, m. p. 89°.

When aniline reacted with S-*p*-toluidinotrichloromethylthiol and with S-*p*-chloroanilinotrichloromethylthiol, triphenylguanidine was obtained in yields of 60 and 62%, respectively, the course of the reaction between amines and arylaminotrichloromethylthiols being thus further confirmed.

S-*Phenoxytrichloromethylthiol*, $PhO \cdot S \cdot CCl_3$.—Phenol (25 g.) in 2N-sodium hydroxide (200 ml.) was treated at intervals with 5 g. portions of thiocarbonyl tetrachloride (40 g. in all), the solution being cooled and shaken between each addition. After 15 minutes an oil was extracted

in ether (180 ml.) and washed twice with water. Having been dried over anhydrous potassium carbonate, the ether was removed at 15° in a vacuum, leaving S-*phenoxytrichloromethylthiol* as a pale yellow oil of characteristic odour, b. p. 196°/760 mm. (decomp.), which was distilled in a high vacuum (Found : S, 13·3. $C_7H_5OCl_3S$ requires S, 13·1%).

The following analogues were prepared : p-*tolyloxy*-, pale yellow oil, b. p. 183°/755 mm. (decomp.) (Found : S, 12·6. $C_8H_7OCl_3S$ requires S, 12·4%); 2-*chlorophenoxy*-, pale yellow oil, with pungent characteristic odour, b. p. 180°/756 mm. (decomp.) (Found : S, 11·6. $C_7H_4OCl_4S$ requires S, 11·5%); s-*xylyloxy*-, deep yellow oil with pungent odour, unstable and could not be purified; *diphenylyl-2-oxy*-, colourless prisms from ligroin, m. p. 58° (Found : S, 10·3. $C_{13}H_9OCl_3S$ requires S, 10·0%).

Reduction of S-*Phenoxytrichloromethylthiol.*—The thiol was dropped slowly on zinc dust suspended in glacial acetic acid, and the mixture heated until reaction commenced. The gases evolved were swept by a stream of air through (*a*) dilute caustic soda solution, (*b*) alcohol, and (*c*) a freshly prepared solution of isatin (1 mg.) in sulphuric acid (100 ml.). The alkali solution gave an intense violet colour with sodium nitroprusside; the alcoholic solution gave a white precipitate of crystalline mercury methyl mercaptide with alcoholic mercuric chloride solution, and the isatin solution turned green, these reactions indicating the presence of methylthiol, the characteristic odour of which was also apparent.

Triphenylguanidine.—S-Phenoxytrichloromethylthiol, prepared as already described, in ligroin (200 ml.) was boiled with aniline (25 g.) for 5 hours. The solid which separated was extracted with boiling water and with boiling dilute hydrochloric acid. The cooled extracts deposited s-triphenylguanidine hydrochloride, which gave 9 g. of the base, pale yellow needles from alcohol, m. p. and mixed m. p. 143°.

The following analogues gave triphenylguanidine and tri-*p*-tolylguanidine by reaction with aniline and *p*-toluidine, respectively :

Trichloromethylthiol.	% Yield of triphenylguanidine.	% Yield of tri-*p*-tolylguanidine.
S-*p*-Tolyloxy-	46	40
S-*o*-Chlorophenoxy-	46	24
S-Xylyloxy-	50	—
S-Phenoxy-	60	43
S-Diphenylyl-2-oxy-	50	—

Phenylthiocarbimide.—Aniline (14 g.), dissolved in hydrochloric acid (1·5 l.; 2 pts. conc. acid and 5·5 pts. water), was stirred with stannous chloride (105 g.). When the latter had completely dissolved, thiocarbonyl tetrachloride (60 g.) was slowly dropped in. Stirring was continued for 7 hours, and the mixture distilled in steam after 24 hours. Phenylthiocarbimide was obtained as a pale yellow oil, b. p. 222° (yield, 70%). The following analogues were also prepared : *p*-chlorophenyl-, yield 99%; *p*-phenetyl-, yield 66%; *m*-2-xylyl-, yield 53%; *m*-tolyl-, yield 72%; 2 : 4-dibromophenyl-, yield 75%; *p*-tolyl-, yield 62%; *p*-anisyl-, yield 47%; 3-carboxyphenyl-, yield 70%. The method is unsuitable for obtaining thiocarbimides from semialiphatic amines (*e.g.*, benzylamine), nitroamines, and naphthylamines.

Thiocarbonyl Chloride.—Hydrochloric acid (12%; 16 l.), stannous chloride (1120 g.), thiocarbonyl tetrachloride (640 g.), and tetrachloroethane (1·5 l.) were vigorously stirred for 3 hours. The tetrachloroethane layer was syphoned off, dried over calcium chloride, and fractionated. Thiocarbonyl chloride passed over at 72—74°. Yield, 255 g. (64% of the theoretical).

151. *Experiments on the Synthesis of Rotenone and its Derivatives. Part V. The Constitution of* apoToxicarol.

By REGINALD G. HEYES and ALEXANDER ROBERTSON.

FROM the work of Clark (*J. Amer. Chem. Soc.*, 1930, **52**, 2461; 1931, **53**, 2264; 1932, **54**, 1600, 2537) and of Butenandt and Hilgetag (*Annalen*, 1932, **495**, 172; 1933, **506**, 162) it is reasonably certain, as has been suggested by these authors, that toxicarol, $C_{23}H_{22}O_7$, possesses a chromanochromanone nucleus of the rotenone type which can be oxidised to

the dehydro-form (chromenochromone). Further, it can be degraded to derric acid and to dehydronetoric acid and hence the chromano-residue is identical with that present in the rotenone molecule. Unlike rotenone, however, toxicarol on hydrolytic fission with warm 5% alkali solution sheds the elements C_5H_6, yielding *apo*toxicarol, $C_{18}H_{16}O_7$, which is considered by Clark (*loc. cit.*) to retain the chromanochromanone nucleus and by the standard procedure can be converted into dehydro*apo*toxicarol, $C_{18}H_{14}O_7$. It must be remembered, however, that the partial formulæ which have been suggested for toxicarol, *apo*-, and dehydro*apo*-toxicarol (*loc. cit.*) rest entirely on analogy with the behaviour of rotenone, deguelin, and tephrosin; moreover, the nature of the phenol present in the chromanone residue of toxicarol has not been determined.

By analogy with the naturally occurring members of the flavone, flavanone and *iso*-flavone series it seemed to us likely that toxicarol contained a phloroglucinol residue in place of the resorcinol nucleus present in rotenone, deguelin, and tephrosin. Accordingly, on approaching the problem of the constitution of toxicarol and its main degradation products from the synthetical side, we assumed that dehydro*apo*toxicarol had formula (II, R = H) and, therefore, in the first place attempted its synthesis by the general method developed in Parts III and IV (J., 1933, 489, 1163).

The condensation of methyl 4 : 5-dimethoxyphenoxyacetate-2-acetonitrile with phloroglucinol gave rise to the *keto-acid* (I, R = H) in comparatively good yield, but attempts to effect cyclisation of this compound in the usual manner were unsuccessful. Similarly, using phloroglucinol dimethyl ether, we obtained the *keto-acid* (I, R = Me), but likewise this compound apparently cannot be readily converted into (II, R = Me). The orientation of (I, R = Me) depends on its ferric chloride reaction, a test which has been found to be diagnostic for ketones of this type derived from phloroglucinol dimethyl ether (Robertson and collaborators, J., 1930, 21; 1931, 1245, 1704).
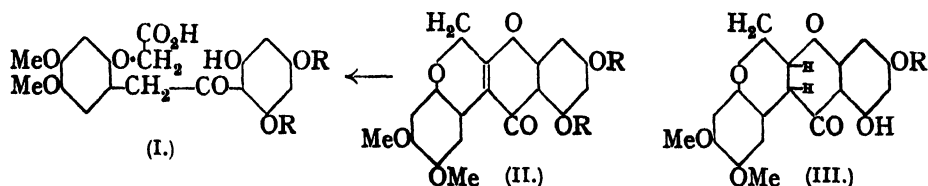
As there did not seem to be an immediate prospect of effecting the synthesis of (II, R = H), we turned our attention to a study of the hydrolytic fission of dehydro*apo*toxicarol. Under the usual conditions whereby members of the dehydrorotenone series and even dehydrodihydrotoxicarol itself are converted into acids of the derrisic acid type (I), dehydro-*apo*toxicarol is decomposed completely, but ultimately, by short treatment with warm 2% aqueous sodium hydroxide, we were able to convert the compound into the keto-acid (I, R = H), identical with the synthetic material. This result makes it clear that dehydro-*apo*toxicarol has the structure (II, R = H), in agreement with the fact that it forms a *diacetate*, and hence *apo*toxicarol may be represented by formula (III, R = H). Further, with methyl sulphate, *apo*toxicarol gives only a monomethyl ether (compare Clark, *loc. cit.*) and, since it is well known that in compounds of the type (III, R = H) a chelate system obtains and the hydroxyl in the *o*-position to the carbonyl group is difficult to methylate, this ether has the orientation (III, R = Me), which is supported by the fact that the compound gives a ferric chloride reaction.

By analogy with the other members of this series it is reasonably certain that the residue C_5 lost in the formation of *apo*toxicarol from toxicarol with the simultaneous generation of a new hydroxyl group has the isoprene skeleton. As has already been remarked by Clark (*loc. cit.*), methylation and acetylation experiments with *apo*toxicarol, toxicarol, and dehydro*apo*toxicarol, as well as the ferric chloride reaction of toxicarol, make it clear that the free phenolic hydroxyl group in toxicarol is in the *o*-position to the carbonyl group, *i.e.*, position 5 in *apo*toxicarol, thus accounting for the insolubility in dilute aqueous sodium hydroxide. Hence the C_5 residue in toxicarol is linked at the 7-hydroxyl group of

*apo*toxicarol. Since toxicarol contains only one ethylenic linkage, this residue, C_5H_8,* is not present as an ether of the type (IV) but forms part of a ring system (types V, VI, VII, or VIII).

(IV.) (V.) (VI.)

(VII.) (VIII.)
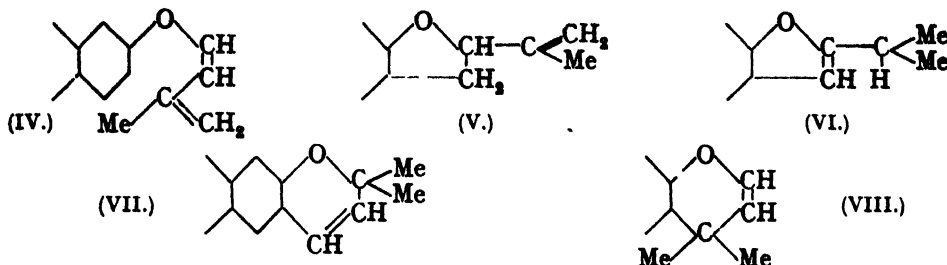
The presence of a dihydrofuran residue of the tubaic acid type (V) as in rotenone is excluded because, unlike rotenone, toxicarol or dihydrotoxicarol cannot be reduced to give phenols of the rotenonic acid type by opening of the dihydrofuran ring and because toxicarol does not isomerise in the presence of mineral acid to give an *iso*toxicarol. A structure of the type (V), as well as the furan type (VI), is also excluded by the fact that the hydrolytic fission of toxicarol is accompanied, as we have now shown, by the formation of acetone. The benzofuran usneol, containing a phloroglucinol nucleus, is stable to alkali under similar conditions (Curd and Robertson, J., 1933, 714, 1173), and in any case fission of a furano-compound of the type (VI) would be expected to give *iso*butyric acid and not acetone.

On the other hand, the formation of acetone can be readily explained on the basis of ring systems of the *gem*-substituted chromen types (VII) and (VIII). By analogy with deguelin (J., 1932, 1380), which on treatment with hot alkali has now been found to give rise to acetone, it would seem not unlikely that toxicarol embodies the 2 : 2-dimethyl-Δ^3-chromen residue (VII) and that the production of acetone by hydrolytic fission of both deguelin and toxicarol follows the lines suggested by Heilbron and his co-workers (J., 1927, 2007) for the decomposition of 2 : 2-diphenyl-Δ^3-chromens.

(IX.) (X.) (XI.) (XII.)
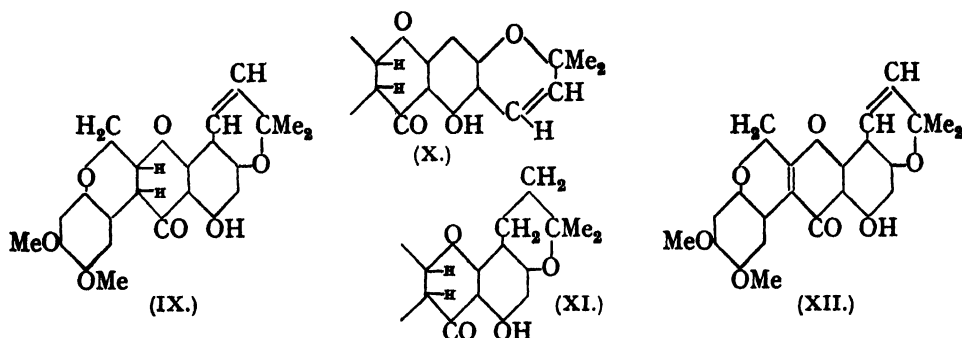
We therefore tentatively suggest that toxicarol is represented by formula (IX) or (X), *i.e.*, 5-hydroxydeguelin type (J., 1932, 1384). Further, dihydro- and dehydro-toxicarol are similarly related to the corresponding deguelin derivatives and may be represented by structures typified in formulæ (XI) and (XII) respectively.

The toxicarol used was prepared by the method of Cahn and Boam (*J. Soc. Chem. Ind.*, 1935, **54**, 42T) from " Sumatra-type " resin, for which we are much indebted to Messrs. Cooper, McDougall, and Robertson, Ltd., London.

EXPERIMENTAL.

4 : 5-*Dimethoxyphenoxyacetic Acid-2-phloracetophenone* (I, R = H).—A mixture of powdered methyl 4 : 5-dimethoxyphenoxyacetate-2-acetonitrile (J., 1933, 1163) (3·8 g.), anhydrous

* The formation of *apo*toxicarol from toxicarol entails a net loss of the elements C_5H_6 and, therefore, the C_5 skeleton in this ring system must carry 8 H atoms.

phloroglucinol (7 g.), and fused zinc chloride (4 g.) in anhydrous ether (150 c.c.) was slowly saturated with hydrogen chloride with occasional shaking; after 8—9 hours the solid suspension was replaced by a thick, dark brown oil. Six days later the ethereal layer was decanted and the syrupy residue was washed five times with dry ether (100 c.c.) and heated with water (150 c.c.) on the steam-bath for 3 hours. Next day the solid product was collected, well washed, and extracted with aqueous sodium bicarbonate (50 c.c.). Acidification of the extract with hydrochloric acid precipitated the *keto-acid* as a reddish solid, which crystallised from 60% aqueous acetone (charcoal) as a *dihydrate* in colourless diamond-shaped plates, m. p. 215° (decomp.) (Found : loss on drying at 105° in a high vacuum, 8·5. $C_{18}H_{18}O_9,2H_2O$ requires H_2O, 8·7%. Found in anhydrous material : C, 56·9; H, 4·7. $C_{18}H_{18}O_9$ requires C, 57·1; H, 4·8%). The compound is sparingly soluble in benzene or ligroin and readily soluble in methyl or ethyl alcohol. With alcoholic ferric chloride it gives a deep red coloration.

4 : 5-*Dimethoxyphenoxyacetic Acid*-2-(2' : 4'-O-*dimethyl*)*phloracetophenone* (I, R = Me).— Ether (150 c.c.) containing methyl 4 : 5-dimethoxyphenoxyacetate-2-acetonitrile (2·7 g.), phloroglucinol dimethyl ether (7 g.), and zinc chloride (4 g.) was saturated with hydrogen chloride and kept for 6 days. After being washed with ether, the oily product was heated with water (150 c.c.) on the steam-bath for 3 hours, and 2 days later acidic material was isolated from the crude solid by means of aqueous sodium bicarbonate; on hydrolysis with 5% hydrochloric acid at 100° the residue insoluble in aqueous sodium bicarbonate gave a further quantity of acid. The *keto-acid* was isolated from material, which had been once crystallised from aqueous methyl alcohol, by 26 extractions with boiling benzene and then purified by repeated crystallisation from 60% methyl alcohol (charcoal), from which it separated in colourless elongated plates, m. p. 196—197° (Found, C, 58·9; H, 5·2. $C_{20}H_{22}O_9$ requires C, 59·1; H, 5·4%). This compound is readily soluble in ethyl acetate, chloroform, and alcohol, and gives a wine-red ferric chloride reaction.

The final residue insoluble in benzene appeared to contain a small amount of the isomeric keto-acid.

Hydrolysis of Dehydroapotoxicarol with Alkali.—The preparation of *apo*toxicarol was carried out according to directions of Clark (*loc. cit.*), but it was found that when the hydrolysis was carried out in an atmosphere of nitrogen the crude product was much cleaner.

A mixture of dehydro*apo*toxicarol (0·1 g.), prepared from *apo*toxicarol by Clark's method (*loc. cit.*), acetic anhydride (1 c.c.), and pyridine (0·5 c.c.) was boiled for 2 minutes and then kept for 24 hours. On isolation the *diacetate* formed pale yellow needles from alcohol–acetic acid, m. p. 202° [Found : C, 61·9; H, 4·4; $CH_3 \cdot CO$, 23·7. $C_{18}H_{12}O_7(CO \cdot CH_3)_2$ requires C, 62·0; H, 4·2; $CH_3 \cdot CO$, 20·2%].

(A) Dehydro*apo*toxicarol (0·5 g.) was refluxed with alcohol (18 c.c.) containing 50% aqueous potassium hydroxide (3·75 c.c.) and zinc dust (0·75 g.) for 1 hour, and the cooled solution acidified with hydrochloric acid and extracted six times with ether. Removal of the solvent left a residue, from which derric acid was isolated by means of aqueous sodium bicarbonate and identified by comparison with an authentic specimen, m. p. and mixed m. p. 168°; a small amount of a phenolic product was isolated with ether from the sodium bicarbonate solution of the crude derric acid.

(B) A suspension of dehydro*apo*toxicarol (0·5 g.) in 2% aqueous sodium hydroxide (18 c.c.) was heated on the water-bath for 20 minutes, cooled, acidified with hydrochloric acid, and kept at 0° for 16 hours. The resulting 4 : 5-dimethoxyphenoxyacetic acid-2-phloracetophenone was purified by means of aqueous sodium bicarbonate and, on crystallisation from aqueous acetone, formed almost colourless, diamond-shaped prisms of the dihydrate identical in every way with an authentic specimen, m. p. and mixed m. p. 214° (Found in material dried over sulphuric acid : C, 52·2; H, 5·2; H_2O, 8·9. Calc. for $C_{18}H_{18}O_9,2H_2O$: C, 52·2; H, 5·3; H_2O, 8·7%. Found in a specimen dried at 105° in a high vacuum : C, 57·4; H, 5·0%).

Hydrolysis of Toxicarol and Deguelin with Alkali.—(A) A solution of toxicarol (3 g.) in absolute alcohol (56 c.c.) and water (45 c.c.) containing potassium hydroxide (22·5 g.) was heated on the water-bath for 3½ hours, cooled, acidified, and distilled on the steam-bath. Treatment of the distillate with 2 : 4-dinitrophenylhydrazine (Brady's method, J., 1931, 756) gave a precipitate of acetone-2 : 4-dinitrophenylhydrazone (1 g.; about 57% of the theoretical), m. p. 124—125°, which formed yellow needles from alcohol, m. p. 127—128°, identical with an authentic specimen.

Hydrolysis of toxicarol (2·2 g.) under the conditions used for the preparation of *apo*toxicarol gave rise to acetone (0·25 g. of 2 : 4-dinitrophenylhydrazone; about 19—20% of the theoretical; the yield of *apo*toxicarol under the same conditions is approx. 10% of the theoretical).

(B) Deguelin (0·2 g.) was refluxed with boiling 33% alcoholic potassium hydroxide (10 c.c.) for

7·5 hours and the acidified solution distilled. Addition of 2 : 4-dinitrophenylhydrazine to the distillate gave a precipitate (0·02 g.) of acetone-2 : 4-dinitrophenylhydrazone. Under less drastic conditions, *e.g.*, heating with 20% alcoholic potassium hydroxide on the steam-bath for 4 hours, acetone is not formed.

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152. *The Transformation of Glucose into Galactose and Gulose by Simple Optical Inversion.*

By JOHN W. H. OLDHAM and GEORGE J. ROBERTSON.

INVESTIGATIONS in this laboratory have for some time been directed towards the elucidation of the mechanism involved in the interconversion of simple isomeric sugars. Light was thrown upon the subject with the discovery that the alkaline hydrolysis of 2 : 3-di-*p*-toluenesulphonyl 4 : 6-dimethyl α-methylglucoside led to the production of a 4 : 6-dimethyl 2 : 3-anhydro-α-methylhexoside along with a 4 : 6-dimethyl α-methylhexoside, which was not a glucose derivative and was tentatively described as a derivative of altrose (Mathers and Robertson, J., 1933, 1076). The natural conclusion to be drawn from this result was that the derivative of altrose owed its formation to Walden inversions within the glucose molecule, which were conditioned by the hydrolysis of the *p*-toluenesulphonyl groups (cf. Phillips, J., 1923, **123**, 44; 1925, **127**, 399).

Cognate researches have shown, however, that such an interpretation is inadequate, since it soon became evident that the alkaline hydrolysis of fully substituted derivatives of glucose containing only one *p*-toluenesulphonyl group was not accompanied by Walden inversion within the molecule. For example, 3-*p*-toluenesulphonyl diacetone glucose gave a quantitative yield of diacetone glucose, and 4-p-*toluenesulphonyl* 6-*trityl* 2 : 3-*dimethyl* α-*methylglucoside* an almost quantitative yield of 6-trityl 2 : 3-dimethyl α-methylglucoside. It was equally significant that the alkaline hydrolysis of 2-p-*toluenesulphonyl* 3-*benzoyl* 4 : 6-*benzylidene* α-*methylglucoside* led to the production of a 4 : 6-*benzylidene* 2 : 3-*anhydro-α-methylhexoside*, and this in turn, on treatment with sodium methoxide, was converted into a *monomethyl* 4 : 6-*benzylidene* α-*methylhexoside* which was not a derivative of glucose (Griffith and Robertson, unpublished result).

It was therefore suggested (Robertson and Oldham, *Nature*, 1934, **133**, 871) that anhydro-formation may be a necessary precursor to this type of inversion, which follows as a consequence of the opening of the anhydro-ring. It is obvious, however, that inversion is also possible during the formation of the anhydro-linkage. In the examples described above, anhydro-formation was of necessity ethylene-oxidic in character, and the possibility that the opening of other anhydro-linkages may be accompanied by inversion has not yet been examined exhaustively. In this connection it is interesting to note that the hydrolysis of 4-p-*toluenesulphonyl* 2 : 3-*dimethyl* α-*methylglucoside* with aqueous methyl-alcoholic sodium hydroxide solution leads essentially to the production of 2 : 3-dimethyl α-methylglucoside. The presence of a small amount of a substance containing a double bond, probably a glucoseen derivative, has also been demonstrated. This result shows either that the 4 : 6-anhydro-linkage is not produced to any appreciable extent, or that, when produced, it is immediately reopened under the given conditions without inversion. Investigations on the well-known 3 : 6-anhydro-derivative of glucose have not yet been completed.

The above views receive substantial support from the fact that we have succeeded in converting *d*-glucose into *d*-galactose and *d*-gulose * by forming an anhydro-ring between positions 3 and 4 in the glucose chain and subsequently opening the ring under the influence of acid. 2 : 3-Dibenzoyl α-methylglucoside (Mathers and Robertson, *loc. cit.*), on successive treatments with triphenylmethyl chloride and *p*-toluenesulphonyl chloride, yielded

* This sugar, in accordance with the older nomenclature, was described as *l*-gulose in a previous communication (*Nature*, 1935, **135**, 103).

crystalline 4-p-*toluenesulphonyl* 2 : 3-*dibenzoyl* 6-*trityl* α-*methylglucoside* (I).   The substance was identical with that prepared by condensing 4-*p*-toluenesulphonyl 2 : 3-dibenzoyl α-methylglucoside (Bell, J., 1934, 1177) with triphenylmethyl chloride.   On alkaline hydrolysis and subsequent acetylation, (I) was converted into an amorphous *monoacetyl* 6-*trityl anhydro-α-methylhexoside*.   This material was, however, considered to be homogeneous, since an analogous series of experiments proceeding from 4-*p*-toluenesulphonyl 2 : 3-diacetyl β-methylglucoside (Oldham and Rutherford, *J. Amer. Chem. Soc.*, 1932, **54**, 366) led ultimately to the production of a crystalline *monoacetyl* 6-*trityl anhydro-β-methylhexoside*, which, incidentally, appeared to be identical with that described by Muller (*Ber.*, 1934, **67**, 422).   The position of the anhydro-linkage must be either 2 : 4 or 3 : 4, and the ultimate production of a derivative of gulose, which involves inversions on carbon atoms 3 and 4, is almost conclusive proof that the anhydro-linkage is between positions 3 and 4.   The amorphous material may therefore be described as a 2-acetyl 6-trityl 3 : 4-anhydro-α-methylhexoside and must correspond with one or other of the three configurations (II), (III), and (IV) shown below.
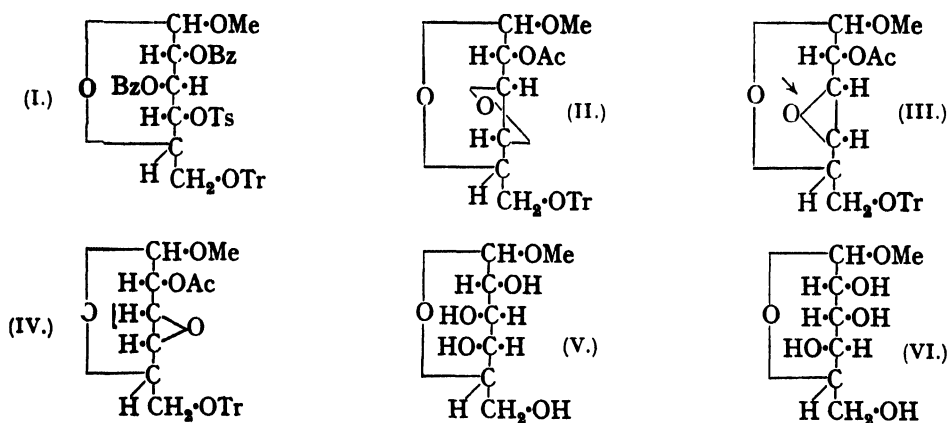
Evidence, which will be published shortly, has been adduced to show that ethylene oxide linkages are not readily formed in the *trans*-position, and structure (II) may therefore be discarded.   Ferns and Lapworth (J., 1912, **101**, 273) have shown that the esters of the sulphonic acids are sharply distinguished from those of the carboxylic acids in their mode of reaction with alkali and alkyl oxides.   The vulnerable point in each series may be represented simply as follows :

$$R—SO_2—O—⋮—R_1 \qquad R—CO—⋮—O—R_1$$

When this conception is considered in conjunction with the work of Phillips (*loc. cit.*), who has shown that the hydrolysis of *p*-toluenesulphonyl esters may be accompanied by change in configuration, it becomes clear that in the alkaline hydrolysis of (I) the configuration on carbon atom number 3 remains intact, while inversion is possible on carbon atom number 4.   It follows that structure (III) is preferable to structure (IV) and the compound under consideration is therefore described as 2-*acetyl* 6-*trityl* 3 : 4-*anhydro-α-methylgalactoside*.

The opening of a 3 : 4 anhydro-linkage in the case under consideration should lead to derivatives of four hexoses, *viz.*, *d*-glucose, *d*-galactose, *d*-gulose, and *d*-allose.   Derivatives of *d*-galactose (V) and *d*-gulose (VI) have actually been isolated, and this indicates that the opening of the anhydro-linkage in (III) takes place as indicated by the arrow.   The configuration on carbon atom number 4 thus remains intact and a partial inversion on carbon atom number 3 explains the formation of derivatives of (V) and (VI).   When (III) was treated with dry hydrogen chloride in acetone solution, the trityl residue was removed, the ethylene oxide ring was opened, and the resulting mixture of monoacetyl methylhexosides condensed with acetone to give a mixture of great complexity.   The

exploration of this mixture is by no means complete and we wish to emphasise the fact that our knowledge of the reaction is still essentially qualitative. With a view to extending this knowledge we have commenced an investigation with compounds possessing the β-configuration, since β-derivatives are notable for their power of crystallisation. Two important facts, however, emerge. We have isolated from the above complex mixture a crystalline *monoacetyl monoacetone α-methylguloside* and a crystalline *monoacetyl monoacetone α-methylgalactoside*. It has not yet been found possible to ascribe definite structures to the above compounds, but the proof of their identity as derivatives of gulose and galactose respectively is fully described in the experimental part of this paper. Further investigation of the complex mixture has led to some indication of the presence of derivatives of allose.

<center>EXPERIMENTAL.</center>

The Alkaline Hydrolysis of 3-p-*Toluenesulphonyl Diacetone Glucose.*—3-*p*-Toluenesulphonyl diacetone glucose (Freudenberg, *Ber.*, 1922, **55**, 935), m. p. 120—121°, (4·35 g.) was dissolved in a hot mixture of alcohol (40 c.c.) and 4·9N-potassium hydroxide (40 c.c.) and boiled for 7 hours. The alcohol was distilled from the clear colourless solution under diminished pressure, the aqueous residue extracted five times with chloroform, and the extracts dried over anhydrous sodium sulphate and evaporated to dryness. The residue (2·67 g.) set spontaneously to a hard mass of crystals (yield, almost quantitative), m. p. 107—108° alone and on admixture with genuine diacetone glucose. The product was recondensed with *p*-toluenesulphonyl chloride, and a good yield of 3-*p*-toluenesulphonyl diacetone glucose obtained.

4-p-*Toluenesulphonyl* 6-*Trityl* 2 : 3-*Dimethyl α-Methylglucoside.*—6-Trityl 2 : 3-dimethyl α-methylglucoside (Robertson, *J.*, 1933, 738), m. p. 169—170°, (10 g.) was dissolved in the minimum amount of pyridine, and *p*-toluenesulphonyl chloride (50% excess) added, followed after 4 days by water and benzene. The benzene layer was washed in succession with dilute hydrochloric acid, water, sodium carbonate solution, and water, dried, and evaporated to dryness. The residue (12·45 g.) crystallised completely and after one crystallisation from absolute alcohol pure 4-*p*-*toluenesulphonyl* 6-*trityl* 2 : 3-*dimethyl α-methylglucoside* was obtained in coarse needles, m. p. 146—147°, $[α]_D$ + 66·3° in chloroform ($c = 1·056$) (Found : OMe, 15·1. $C_{35}H_{38}O_8S$ requires OMe, 15·05%).

The Alkaline Hydrolysis of 4-p-*Toluenesulphonyl* 6-*Trityl* 2 : 3-*Dimethyl α-Methylglucoside.*—The material (5·6 g.) was dissolved in benzene (50 c.c.), and a solution of sodium (7·5 g.) in methyl alcohol (100 c.c.) added. The resulting emulsion gave, on heating, a clear solution, which was boiled for 12 hours and cooled. Water and benzene were then added and the benzene layer was washed with dilute hydrochloric acid and with water, dried over anhydrous sodium sulphate, and evaporated. The residue (4·0 g.) crystallised spontaneously. On recrystallisation from absolute alcohol the material had m. p. 169—170°, alone and when mixed with authentic 6-trityl 2 : 3-dimethyl α-methylglucoside. Yield, almost quantitative.

4-p-*Toluenesulphonyl* 2 : 3-*Dimethyl α-Methylglucoside.*—The trityl residue was removed from 4-*p*-toluenesulphonyl 6-trityl 2 : 3-dimethyl α-methylglucoside (28·8 g.) by the method of Helferich and Klein (*Annalen*, 1926, **450**, 222). The product (18·7 g.) was a glass and analysis showed that it still contained triphenylcarbinol or unchanged material. This was in keeping with the fact that the yield was slightly in excess of the theoretical. No practical method of separation was available, so the crude material (18·5 g.) was treated with the mixture obtained by dissolving sodium (18·4 g.) in methyl alcohol (320 c.c.) and adding water (80 c.c.). On heating, the glass dissolved with the exception of a small and apparently crystalline residue, and the mixture was boiled for 9 hours. The methyl alcohol was evaporated, water added after cooling, and the residue of unchanged 4-*p*-toluenesulphonyl 6-trityl 2 : 3-dimethyl α-methylglucoside (4·7 g.) removed. The aqueous filtrate was extracted five times with chloroform; the extracts, after drying over anhydrous sodium sulphate, yielded a mobile syrup (2·0 g., A). The aqueous filtrate, after the addition of solid potassium carbonate, was again extracted five times with chloroform; these extracts yielded a syrup (4·4 g.), which set to a mass of crystals (B).

The syrup A (2·0 g.), $n_D^{15°}$ 1·4744, was dissolved in benzene and extracted repeatedly with water. The residue obtained from the benzene (0·4 g.) contained sulphur and was apparently unchanged material. The aqueous extract was extracted five times with chloroform; the extracts yielded a syrup (0·9 g.), $n_D^{15°}$ 1·4685, which vigorously absorbed bromine and therefore contained an unsaturated substance, probably a derivative of glucoseen. It is possible that the 4 : 6-anhydro-compound was also present in small amount. The aqueous extract was now

treated with solid potassium carbonate and again extracted five times with chloroform; the extracts yielded a syrup (0·4 g.), $n_D^{16°}$ 1·4702; this crystallised and proved to be identical with the crystalline material (B), which, alone or mixed with authentic 2 : 3-dimethyl α-methyl-glucoside (m. p. 80—83°), melted at 81—83°.

4-p-Toluenesulphonyl 2 : 3-Dibenzoyl 6-Trityl α-Methylglucoside.—2 : 3-Dibenzoyl α-methyl-glucoside (28 g.), prepared from 2 : 3-dibenzoyl 4 : 6-benzylidene α-methylglucoside by a slight variation of the method described by Mathers and Robertson (J., 1933, 1079), was dissolved in hot pyridine (20 c.c.), triphenylchloromethane (21 g.) added, and the mixture heated on a boiling water-bath for 2 hours. *p*-Toluenesulphonyl chloride (50% excess) was now added to the hot reaction mixture, which, after complete solution had been effected, was set aside in a warm place for at least 72 hours. The product was isolated in the usual manner and crystallised from absolute alcohol. The yield was variable, usually about 76%, but declined to about 50% on working with larger quantities. *4-p-Toluenesulphonyl 2 : 3-dibenzoyl 6-trityl α-methylglucoside* crystallised in prisms, m. p. 163—164°; $[α]_D + 66·3°$ in chloroform ($c = 2·044$). It was soluble in acetone, benzene, chloroform, and ether, but sparingly soluble or insoluble in other solvents (Found : OMe, 4·0. $C_{47}H_{42}O_{10}S$ requires OMe, 3·9%. 0·1412 G. used 5·3 c.c. of $N/10$-sodium hydroxide. Calc., 5·3 c.c.).

2-Acetyl 6-Trityl 3 : 4-Anhydro α-methylgalactoside.—When the above compound was boiled with $2N$-sodium hydroxide (1 part, 10% excess), water (2 parts), and acetone (4 parts) for 1 hour, a homogeneous solution was obtained. This, made definitely alkaline by the addition, if necessary, of more sodium hydroxide solution, was boiled for another 30 minutes, the acetone distilled under diminished pressure, the residue extracted with benzene, and the extract washed with water. The product obtained on evaporation of the benzene was a glass which, treated with acetic anhydride in pyridine solution, gave in almost theoretical yield a product which could not be crystallised and had the empirical composition of a monoacetyl trityl anhydro-α-methylhexoside. The above structure has been ascribed to it (Found : OMe, 6·2; CH_3·CO, 8·5. $C_{28}H_{28}O_6$ requires OMe, 6·7; CH_3·CO, 9·3%).

The Partial Hydrolysis of 2-Acetyl 6-Trityl 3 : 4-Anhydro-α-methylgalactoside in Acetone containing Dry Hydrogen Chloride.—Dry hydrogen chloride (17 g.) was passed into a cooled solution of the material (71 g.) in acetone (200 c.c.), the mixture was kept for 1 hour at room temperature, and after neutralisation with silver carbonate, filtration, and evaporation to small bulk, the residue was poured into water containing a little pyridine. After a few minutes the precipitated triphenylcarbinol was filtered off, and the filtrate extracted six times with chloroform, which removed a syrup (A) (27·7 g.). The aqueous solution was shaken with silver carbonate to remove traces of chlorine, treated with hydrogen sulphide, filtered, and evaporated to dryness; the residue, treated with acetone, gave immediately a crystalline monoacetyl methylhexoside (2·9 g.) (Found : OMe, 12·9; CH_3·CO, 18·0. $C_9H_{16}O_7$ requires OMe, 13·1; CH_3·CO, 18·3%). The material was, however, obviously a mixture, since it had m. p. 145—160°. It showed $[α]_D + 123·5°$ in water ($c = 1·525$) and on alkaline, followed by acid, hydrolysis the rotation became $+ 158°$ and $+ 48·3°$ respectively (after allowing for changes in concentration). In spite of the close approximation of these figures to those of glucose, no tetra-acetyl α-methylglucoside was obtained on submitting the material to acetylation, and no α-methylglucoside on deacetylation. In view of what follows it seems probable that this material represents a mixture of gulose and galactose derivatives.

The remainder of the material from the original aqueous solution (5·5 g.) consisted of a syrup which reduced Fehling's solution distinctly and has not been further investigated (Found : OMe, 9·6; CH_3·CO, 21·0%).

Examination of the chloroform extract (A). The syrup (27·7 g.), on treatment with ether, immediately deposited a crystalline substance, which was washed with ether (B, 3·3 g.); the mother-liquors on longer standing deposited a different crystalline substance (C, 4·9 g.). The residue (D, 19 g.) was a syrup which showed no further signs of crystallisation.

Examination of the crystalline material (B). The material was homogeneous, m. p. 176—178°, showed $[α]_D + 76·8°$ in chloroform ($c = 3·796$), and was insoluble in light petroleum, practically insoluble in ether, sparingly soluble in water, and soluble in other solvents. It was shown to be a *monoacetyl monoacetone α-methylguloside* (Found : OMe, 11·3; CH_3·CO, 15·4. $C_{12}H_{20}O_7$ requires OMe, 11·2; CH_3·CO, 15·5%). The substance was deacetylated with boiling aqueous sodium hydroxide, and extraction with chloroform after addition of potassium carbonate gave *monoacetone α-methylguloside* in 98% yield; prisms, m. p. 132—133°, $[α]_D + 88·5°$ in chloroform ($c = 3·349$) (Found : OMe, 13·2. $C_{10}H_{18}O_6$ requires OMe, 13·2%).

The above monoacetone α-methylguloside was hydrolysed with $N/50$-sulphuric acid to

remove the acetone group, but it was unexpectedly found that the methylgulosidic group was being removed at the same time. The reaction was therefore continued until equilibrium was attained (8 hours), the rotation changing from $+ 94 \cdot 7°$ to $- 17 \cdot 9°$ (allowing for change of concentration), and the free sugar was isolated by neutralising the reaction mixture with barium carbonate, evaporating it to dryness, and extracting the residue with methyl alcohol. In this way a syrup was obtained, which was converted into gulosazone, m. p. 156°. The specific rotation of gulose is given as $- 20 \cdot 4°$ (Blanksma and van Ekenstein, *Centr.*, 1908, II, 1583).

Examination of the crystalline material (C). This material, isomeric with the material (B), consisted of prisms, m. p. 101—102°, was considerably more soluble, and showed $[\alpha]_D + 127 \cdot 3°$ in chloroform ($c = 3 \cdot 034$). It was shown to be a *monoacetyl monoacetone α-methylgalactoside* (Found : OMe, 11·1; $CH_3 \cdot CO$, 17·1. $C_{13}H_{20}O_7$ requires OMe, 11·2; $CH_3 \cdot CO$, 15·5%). On deacetylation in the same manner as before, it yielded monoacetone α-methylgalactoside in theoretical yield, prisms, m. p. 102—104° (this m. p. was mistakenly given as 109—110° in *Nature*, 1935, 135, 103), $[\alpha]_D + 147 \cdot 9°$ in chloroform ($c = 1 \cdot 18$), $+ 168 \cdot 6°$ in water ($c = 1 \cdot 091$) (Found : OMe, 12·8. Calc. for $C_{10}H_{18}O_6$: OMe, 13·2%).

Monoacetone α-methylgalactoside was submitted to partial hydrolysis with 10% aqueous acetic acid; the rotation changed from $+ 175 \cdot 1°$ to $+ 179 \cdot 5°$ in 45 minutes (allowing for change of concentration). Acetone was detected in the distillate by means of the iodoform reaction. The product (98% yield) crystallised completely and after recrystallisation from absolute alcohol did not depress the m. p. of authentic α-methylgalactoside. It showed $[\alpha]_D + 175 \cdot 5°$ in water ($c = 1 \cdot 068$). Fischer (*Ber.*, 1895, 28, 1157) gives $[\alpha]_D + 179°$ for α-methylgalactoside. Confirmatory proof of its identity was obtained by acid hydrolysis, the rotation falling to $+ 76 \cdot 6°$ (allowing for change of concentration). The rotation of galactose in water is $+ 81°$. This was followed by the conversion of the free sugar into galactosazone (m. p. and mixed m. p.) and by the formation of the anilide of galactose, m. p. 151°, mixed m. p. 151°.

Examination of the residue (D). This is involved and by no means complete. After deacetylation by means of sodium hydroxide solution at the ordinary temperature, monoacetone α-methylgalactoside (2·0 g.) and monoacetone α-methylguloside (0·6 g.) were isolated. When monoacetone α-methylgalactoside is hydrolysed with $N/50$-hydrochloric acid, the rotation indicates that 58% of the material is hydrolysed to the free sugar in 8 hours, whereas the corresponding derivative of gulose is completely hydrolysed in a similar period. A further attempt to isolate α-methylguloside from monoacetone α-methylguloside by hydrolysis with 5% aqueous acetic acid resulted in a partial removal of the gulosidic methyl group. The problem was finally solved by using $N/500$-sulphuric acid in the hydrolysis. The rotation changed to a final value of $+ 111 \cdot 9°$ in 2¼ hours (allowing for change of concentration). α-*Methylguloside*, isolated in the usual way, was a syrup, $[\alpha]_D + 109 \cdot 7°$ in water ($c = 1 \cdot 184$) (Found : OMe, 15·8. $C_7H_{14}O_6$ requires OMe, 15·9%), which after solidifying crystallised from ethyl acetate in prisms, m.p. 77—79°.

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153. *The Rate of Decomposition of Some* p-*Substituted Nitrosoacetanilides in Benzene.*

By WILLIAM S. M. GRIEVE and DONALD H. HEY.

THE rate of decomposition of benzenediazonium salts and its relationship to the presence and position of substituent groups in the aromatic nucleus have attracted the attention of many workers (Hirsch, *Ber.*, 1891, 24, 324; Hausser and Muller, *Compt. rend.*, 1892, 114, 549, 669, 760, 1438; Oddo, *Gazzetta*, 1895, 25, 327; Oddo and Ampola, *ibid.*, 1896, 26, 541; Hantzsch, *Ber.*, 1900, 33, 2517; Hantzsch and Thompson, *Ber.*, 1903, 41, 3519; Euler, *Annalen*, 1902, 325, 292; Cain and Nicoll, J., 1902, 81, 1412; 1903, 83, 206, 470; Yamamoto, *J. Soc. Chem. Ind. Japan*, 1929, 32, 279, 308, 352; 1930, 33, 177, 231, 358; 1932, 35, 11, 298, 564; 1933, 36, 59, 490, 609; 1934, 37, 29, 400, 512; Snow, *Ind. Eng. Chem.*, 1932, 24, 1420). From the results of these investigations, it is possible to construct

a series in order of stability,.and, with reference to the following substituent groups in the aromatic nucleus, the order of decreasing stability is : p-OMe, p-Cl, p-Br, p-Me, H, m-Me. The most striking feature of these results is the magnitude of the differences in stability which they reveal. These differences are sufficiently large to render impracticable the measurement of the velocities of decomposition for the complete series at any one temperature, but by extrapolation the following comparative figures can be obtained (based on Euler's measurements), the velocity constant for p-methoxybenzenediazonium chloride, the most stable member of the series selected, being taken as unity : p-OMe 1, p-Cl 12·5, p-Br 22·5, p-Me 149·5, H 2241, m-Me 6640.

On the other hand, little attention has been paid to the rates of decomposition of the sodium diazoate of benzene and substituted benzenes, but recent observations by Blumberger (*Rec. trav. chim.*, 1930, **49**, 276), Jolles (*Atti R. Accad. Lincei*, 1932, **15**, 292, 395), and Oddo and Indovina (*Gazzetta*, 1932, **62**, 1119, 1138) have shown that the decomposition in alkaline solution is of a more complicated nature. Nevertheless, Jolles and Camiglieri (*ibid.*, p. 720) investigated the rates of decomposition of sodium benzenediazoate and a somewhat limited series of substituted benzenediazoates, and found that the order of stability was the reverse of that which obtains in the diazonium salt series. No velocity
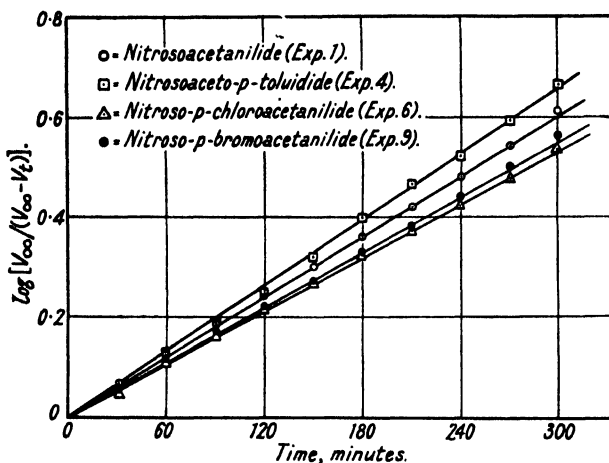
constants were calculated, but the following decreasing order of stability was revealed : m-Me, H, p-Me, p-OMe. Although the reversal in the order of stability is complete, the exact significance of these measurements is somewhat obscure, owing to their dependence on the alkalinity of the medium (cf. Blumberger, *loc. cit.*; Oddo and Indovina, *loc. cit.*) and to the possibility of the transformation of the normal (*syn*)-diazoates into the more stable *iso*(*anti*)-diazoates.

Velocity measurements have now been made for the decomposition of nitrosoacetanilide and a series of substituted nitrosoacetanilides, which may be in tautomeric equilibrium with the acetyl derivatives of the corresponding diazoates : $Ar\cdot N(NO)\cdot CO\cdot CH_3 \rightleftharpoons Ar\cdot N\colon N\cdot O\cdot CO\cdot CH_3$. The velocity of decomposition of nitrosoacetanilide itself in a series of solvents has already been measured, and the reaction found to be unimolecular or quasi-unimolecular (Grieve and Hey, J., 1934, 1797). The number of substituted nitrosoacetanilides available for study is confined to those prepared from p-toluidine and p-bromo- and p-chloro-aniline. Since attempts to prepare other nitrosoacetanilides were unsuccessful (see p. 691), direct comparison with the results of Jolles and Camiglieri on the sodium diazoates cannot be made.

Quantitative measurements of the rate of decomposition of the nitroso-derivatives of acetanilide, aceto-p-toluidide, and p-chloro- and p-bromo-acetanilide in benzene were carried out by observing the rate of evolution of nitrogen. In each case, good unimolecular velocity constants were obtained, all of which, however, fall within a small range, as shown in the accompanying diagram, which represents the course of the reactions up

to 75—80% of completion. In the four examples studied, the order of decreasing stability is *p*-Cl, *p*-Br, H, *p*-Me. These results are in marked contrast to the much larger differences observed between the velocity constants for the decomposition of the corresponding diazonium salts.

EXPERIMENTAL.

Nitrosoacetanilide (m. p. 50—51°) was prepared by passing nitrous fumes into a solution of acetanilide in glacial acetic acid and precipitating the product with water (Grieve and Hey, *loc. cit.*). Nitrosoaceto-*p*-toluidide, m. p. 80° (Fischer, *Ber.*, 1877, **10**, 959; Kliegl and Huber, *Ber.*, 1920, **53**, 1655), nitroso-*p*-chloroacetanilide, m. p. 83—84° (Bamberger, *Ber.*, 1897, **30**, 368; Bamberger and Baudisch, *Ber.*, 1909, **42**, 3589), and nitroso-*p*-bromoacetanilide, m. p. 88° (Bamberger, *loc. cit.*; Bamberger and Baudisch, *loc. cit.*; Hantzsch and Wechsler, *Annalen*, 1902, **325**, 242) were prepared in similar manner.

The measurements of the rate of evolution of nitrogen for solutions of the four nitrosoacetanilides in pure thiophen-free benzene, previously saturated with nitrogen, were carried out at 20° in the apparatus previously described (Grieve and Hey, *loc. cit.*). The quantity of the nitroso-compound dissolved in 100 c.c. of benzene was equivalent to 2·000 g. of nitrosoacetanilide in order that the total nitrogen content might be the same in each case. About 20—30 c.c. of nitrogen were allowed to escape before half-hourly readings were taken over a period of 6—7 hours, and the final volume of nitrogen was read after the lapse of at least 24 hours. The volumes of gas evolved were corrected, and the results obtained by plotting $\log [V_\infty/(V_\infty - V_t)]$ against t, where V_∞ is the final observed volume and V_t the volume at time t, are shown in the diagram. The total volumes of nitrogen liberated from the different nitrosoacetanilides, which vary from about 75 to 90%, for nitrosoaceto-*p*-toluidide and nitrosoacetanilide respectively, together with the unimolecular velocity constants, given by the equation $k = 2·303/t \cdot \log V_\infty/(V_\infty - V_t)$, are shown in the following table :

	Nitrosoacetanilide in 100 c.c. benzene.	Wt. of solute, g.	Vol. of N_2 evolved, c.c.	N_2 evolved, %.	$k.10^3$.
1.	Unsubstituted	2·0000	248·0	90·8	4·61
2.	,, ...	2·0000	247·8	90·7	4·59
3.	,, ...	2·0000	240·5	88·0	4·53
4.	*p*-Methyl	2·1707	206·2	75·5	5·02
5.	,, ...	2·1707	203·7	74·6	4·96
6.	*p*-Chloro	2·4209	240·7	88·1	4·09
7.	,, ...	2·4209	241·5	88·4	4·15
8.	,, ...	2·4209	243·1	89·0	4·08
9.	*p*-Bromo-	2·9634	216·5	79·3	4·24
10.	,, ...	2·9634	224·2	82·1	4·22

Attempts to prepare the nitroso-derivatives of other acetylated bases by the method outlined above were unsuccessful. In the case of *p*-nitroacetanilide the dark green solution, obtained on passing nitrous fumes into a solution of the anilide in glacial acetic acid, evolved oxides of nitrogen when poured into water and *p*-nitroacetanilide was precipitated. With aceto-*m*-toluidide a yellow oil separated when the reaction mixture was poured into water, but before separation could be effected nitrogen was freely evolved with the formation of a black tar. With the acetyl derivatives of *o*-chloroaniline, *p*-anisidine, and α- and β-naphthylamine, dark oily products were precipitated, from which nitrogen was freely evolved. The yellow oil, which separated when the reaction mixture from aceto-*p*-phenetidide was poured into water, was extracted with ether, on evaporation of which yellow needles separated. There was no evolution of nitrogen. Recrystallisation from water or dilute alcohol gave 3-nitro-4-acetamidophenetole, m. p. 103° (Wender, *Gazzetta*, 1889, **19**, 219), which was identified by hydrolysis with concentrated hydrochloric acid to 3-nitro-4-aminophenetole, red prisms, m. p. 112° (cf. Wender, *loc. cit.*), and by nitration with fuming nitric acid at 0—5° to 2 : 3-dinitro-4-acetamidophenetole, yellow needles, m. p. 206° (cf. Wender, *loc. cit.*; Blanksma, *Rec. trav. chim.*, 1908, **27**, 49).

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154. *Properties of the Oxides of Nitrogen. Part I. The Binary System* N_2O_4–N_2O_5.

By T. Martin Lowry and John T. Lemon.

Preparation and Purification of Nitric Anhydride.

Nitric anhydride, first prepared by the action of dry chlorine on silver nitrate (Deville, *Ann. Chim. Phys.*, 1850, **28**, 241), was afterwards generally made by the action of phosphoric anhydride on nitric acid (Weber, *J. pr. Chem.*, 1872, **6**, 342; Pogg. *Ann.*, 1872, **147**, 113; Berthelot, *Bull. Soc. chim.*, 1874, **21**, 53; *Ann. Chim. Phys.*, 1875, **6**, 203). The distillate obtained by heating the mixture separates into two layers, of which the upper one crystallises when cooled, after which a partial purification of the crystals may be effected by pouring off the mother-liquor and repeating the crystallisation; but the material thus produced is not usually pure enough for physicochemical measurements. For instance, in our experiments, two samples, prepared by dehydration under reduced pressure, were apparently free from nitric acid, but the third sample, in a mixture containing 74% N_2O_4, became turbid when cooled to $-8°$ and was obviously hydrated. Since the yields of the anhydride were always poor (10—20%), and it was found difficult to remove the last traces of nitric acid, even by sublimation through a tube of phosphoric oxide in a stream of ozonised oxygen (Russ and Pokorny, *Sitzungsber. Akad. Wiss. Wien*, 1913, **122**, 439; *Monatsh.*, 1913, **34**, 1027), the dehydration method was abandoned in favour of direct ozonisation of nitrogen peroxide (Helbig, *Atti R. Accad. Lincei*, 1902, **11**, ii, 311; 1903, **12**, i, 211). Quantities of 2—3 g. can thus be prepared very conveniently, with a yield of about 30—40% of the ozone supplied. The materials used in this preparation are all anhydrous; but great care was needed to exclude all traces of moisture from the apparatus, since it was almost impossible to get rid of nitric acid when it had once appeared in the system.

Helbig's method appears to depend on two consecutive reactions : $NO_2 + O_3 = NO_3 + O_2$ and $NO_2 + NO_3 = N_2O_5$ (Schumacher and Sprenger, *Z. physikal. Chem.*, 1929, *A*, **140**, 281; cf. Sprenger, *ibid.*, 1928, **136**, 49). It has the advantage that the lower oxides produced by the decomposition of nitric anhydride, $N_2O_5 = N_2O_3 + O_2$ and $N_2O_3 + N_2O_5 = 4NO_2$, but not $N_2O_5 = NO_2 + NO_3$, are immediately reoxidised instead of having to be removed by fractional distillation. On the other hand, since the hyperoxide (NO_3?) is only formed in presence of ozone, and probably interacts with nitrogen peroxide to form nitric anhydride, it is not likely to persist as an impurity in the solid product.

Melting Point of Nitric Anhydride.—The m. p. of nitric anhydride was given as $30° \pm 1°$ by four of the earlier authors (Deville; Weber; Berthelot; Helbig; *locc. cit.*). On the other hand, Russ and Pokorny (*loc. cit.*) attribute this m. p. to the presence of nitric acid or to the formation of nitrogen peroxide, and conclude that the pure material passes directly from the solid into the vapour state. Their experiments were made with nitric anhydride, which had been sublimed, from a mixture of nitric acid and phosphoric oxide, through a tube of phosphoric oxide, in a current of ozonised oxygen, and condensed in a glass receiver cooled to $-80°$. Specimens of 1—2 g., condensed in glass tubes, sealed, and stored at a low temperature, became liquid in 9 mins. at $34°$, and in 15 mins. at $30·5°$, but never gave a well-defined m. p., although in each case the necessary heat-transfer was complete in 3—4 mins. Analysis of a sample which had thus been melted at 30—$30·5°$ showed the presence of 6% N_2O_4. A sample of 1 g., prepeared by Helbig's method, in a U-tube protected from the air by phosphoric oxide, sublimed rapidly at $35°$ but was not observed to melt.

Daniels and Bright (*J. Amer. Chem. Soc.*, 1920, **42**, 1131) also observed that 5 g. of nitric anhydride, resublimed in a current of ozone, and condensed in a glass apparatus, which was then evacuated and sealed, showed signs of melting after 45 mins. at $30°$; but they concluded that " It is not a true melting, but a phenomenon complicated by the dissolving of nitrogen tetroxide in the surface of the crystals." At $35°$ " the contamination with nitrogen tetroxide and the appearance of melting occurs in the first few minutes " (*loc. cit.*, p. 1138).

From their vapour-pressure curves (*Sitzungsber. Akad. Wiss. Wien*, 1913, **122**, 415), Russ and Pokorny deduced, by extrapolation from 17·5°, a sublimation temperature of 34° (*loc. cit.*, p. 447), and concluded that : " Pure N_2O_5 does not exist at atmospheric pressure in a liquid phase." In the same way, Daniels and Bright report that : " The vapour pressure reaches an atmosphere at 32·5°, as shown by a short extrapolation of the curve. The melting-point lies above the sublimation-point, as stated by Russ and Pokorny " (*loc. cit.*, p. 1139).

In our opinion, these results are not conclusive, since experiments in sealed tubes do not allow any adequate opportunity for getting rid of nitrogen peroxide by vaporisation, and, in order to secure a correct m. p., a much more rapid procedure is needed, exactly as in the case of compounds such as benzoylcamphor (Lowry, MacConkey, and Burgess, J., 1928, 1337) which undergo reversible isomeric change when melted. Since a knowledge of the m. p. was required in order to complete the equilibrium diagram, a series of observations was made in which these considerations were kept in view.

In a first series of experiments, the receivers in which the anhydride was condensed were not sealed off, but were filled with dry air and allowed to warm to room temperature. One of the taps being open to the atmosphere, the receiver was then transferred to a bath of water at a temperature a few degrees below the m. p., and heated at a rate of about 1° per min. The initial temperature and rate of heating were noted, in addition to the temperature at which incipient melting (as distinguished from mere sintering) could be seen. As the m. p. was approached, evaporation became rapid and the yellow colour of nitrogen peroxide began to appear, to an extent which depended on the duration of heating. By progressively raising the initial temperature, and thus reducing the time during which decomposition could take place, the m. p. was finally raised above 40°.

Sample.	M. p.	Initial temp. of bath.	Time interval, mins.	Rate of heating.
1	37·3°	28°	9—10	1°/min.
2	38·8	30—31	8—9	,,
3	40·7	36·8	4	,,

Subsequent experiments were based on the assumption that the most trustworthy results would be obtained by determining the m. p. *in presence of ozonised oxygen.* For this purpose, nitric anhydride was condensed in a narrow U-tube, about 3 mm. in internal diameter, which had been drawn out from a wider tube in order to reduce the thickness of the walls. Since it was essential to avoid cooling by the current of ozonised oxygen, the gas was made to pass through a glass coil, immersed in the same water-bath, before entering the U-tube. Under these conditions it was found that, even if an initial melting took place at a temperature as low as 35°, when the water-bath was filled abruptly with tepid water, the wet solid always dried up quickly as soon as a slow current of ozonised oxygen was turned on. The residue appeared to be a highly purified nitric anhydride, from which all traces of decomposition product had been vaporised.

At this stage, a new difficulty presented itself, since it was very difficult indeed to melt this residue in a stream of ozonised oxygen. This difficulty we attributed mainly to cooling by evaporation of the extremely volatile solid. For instance, on one occasion a central core of loose crystals, left at the bottom of one arm of the U-tube, was heated for about 5 mins. at 45°, with continual evaporation, until the ozonised oxygen was turned off, whereupon the material soon sintered and melted at the bottom of the tube. On two occasions, however, a small plug of crystals, which appeared to be exceptionally free from decomposition products, was left at the point of entry of the gas, where the tube was slightly constricted, and where supplies of ozone were most abundant. In a critical experiment, this plug was watched carefully, and was seen to drop through the constriction at a temperature of 41°. This temperature, which agrees with those of the first series, has been used to complete the freezing-point diagram ; but we are not prepared to assert categorically that melting, as contrasted with sublimation, can occur in the complete absence of decomposition products. On the other hand, any m. p. below 40°, can, we think, be rejected as incompatible with adequate purity of the material.

Freezing Points of Mixtures of N_2O_4 and N_2O_5.—A receiver containing a known weight

of the pentoxide was cooled with solid carbon dioxide and acetone, and attached to an apparatus from which a known weight of nitrogen peroxide could be sublimed into it. The receiver was then sealed, and transferred to a large transparent Dewar vessel containing 1—1½ l. of alcohol, which was stirred mechanically and cooled as required by the addition of solid carbon dioxide, or by blowing liquid nitrogen on to the surface (cf. Rupert, *J. Amer. Chem. Soc.*, 1909, **31**, 851). For temperatures above 0°, a water-bath cooled with ice, or controlled by a flow of warm or cold water, was used instead of alcohol. The mixtures were stirred electromagnetically, by a piece of iron sealed into a glass tube and operated by a solenoid (cf. Terrey and Spong, *J.*, 1932, 219).

Nitrogen peroxide crystallised readily from the stirred mixtures in the sealed tubes, with not more than 2—3° of supercooling. It separated in small, bright, heavy, granular crystals, which grew and multiplied rapidly. Slow growth in an undisturbed liquid gave rise to relatively large hexagonal crystals on the walls of the tube; but, when detached, the crystals fell to the bottom, and were not readily carried up by the stirrer, since they were markedly denser than the liquid. The f. p. was recorded as the temperature at which a small quantity of solid peroxide remained in equilibrium with the liquid, without either growing or dissolving.

FIG. 1.
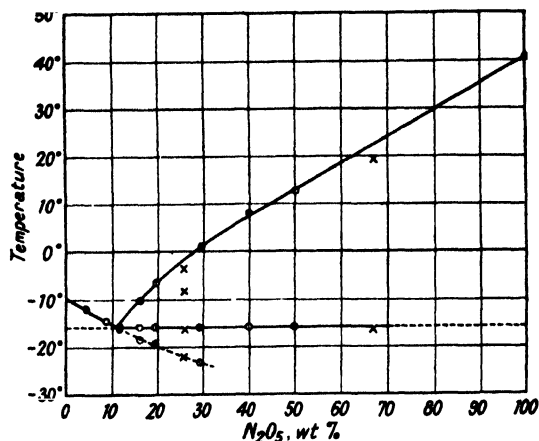
Nitric anhydride exhibited such remarkable supercooling that it was possible to determine the f. p. of nitrogen peroxide far beyond the eutectic temperature. In this way the (metastable) freezing-point curve was extended from 11% to 30% N_2O_5, the supercooling then being 24°. Similar supercooling was noticed by Berl and Saenger (*Sitzungsber. Akad. Wiss. Wien*, 1929, **138**, 1036; *Monatsh.*, 1929, **53**—**54**, 1036) in mixtures of nitric anhydride with anhydrous nitric acid.

On account of this supercooling, it was necessary to initiate crystallisation of nitric anhydride by chilling the liquid either in ice or in carbon dioxide snow and acetone, and then shaking the tube or agitating the liquid with the internal stirrer. The crystals thus formed adhered tenaciously to the sides of the tube, but, when detached, were readily carried up into suspension by the stirrer, and could thus be distinguished easily from crystals of nitrogen peroxide. Slow growth from concentrated solutions gave white needles, similar to those produced by slow condensation from the vapour. The temperature at which a small deposit of nitric anhydride just disappeared, when the tube was allowed to warm in the observation bath at the rate of 0·2—0·3°/min., was taken as the f. p. of the system.

The f. p.'s thus determined are shown in Table I and plotted in Fig. 1. The eutectic temperatures are those at which the first signs of melting could be seen in the completely frozen mixtures. Each temperature is, as a rule, the result of at least three concordant observations.

TABLE I.

Freezing Points of Mixtures of N_2O_5 and N_2O_4.

Composition by wt.		Composition, wt. %.		Eutectic line temp.	F. p.	Solid phase.	F. p.	Solid phase.
N_2O_5, g.	N_2O_4, g.	N_2O_5.	N_2O_4.					
0·1287	2·8669	4·29	95·71	—	−11·8°	N_2O_4	—	—
0·2835	2·9529	8·76	91·24	—	−14·3	,,	—	—
0·2556	1·9077	11·86	88·14	−15·8°	−16·3	,,	—	—
0·4959	2·5813	16·12	83·88	−15·8	−18·2	,,	−10·1°	N_2O_5
0·5871	2·4301	19·46	80·54	−15·6	−19·1	,,	− 6·4	,,
0·9704	2·3404	29·31	70·69	−15·7	−23·2	,,	1·1	,,
1·0624	1·6031	39·86	60·14	−15·8	—	—	8·0	,,
1·6157	1·6122	50·05	49·95	−15·7	—	—	+12·0	,,

The eutectic point is at 10·8% N_2O_5 and − 15·8°, and there is no evidence of the formation of any compound of the two components.

Formation of Two Liquid Layers.—Liquid mixtures of N_2O_4 and N_2O_5 are homogeneous, but readily separate into two layers when contaminated with a small proportion of moisture; *e.g.*, when the anhydride is prepared by dehydrating nitric acid, the distillate gives an upper darker-coloured layer of the two oxides, and a lower layer of nitric acid containing the

FIG. 2.
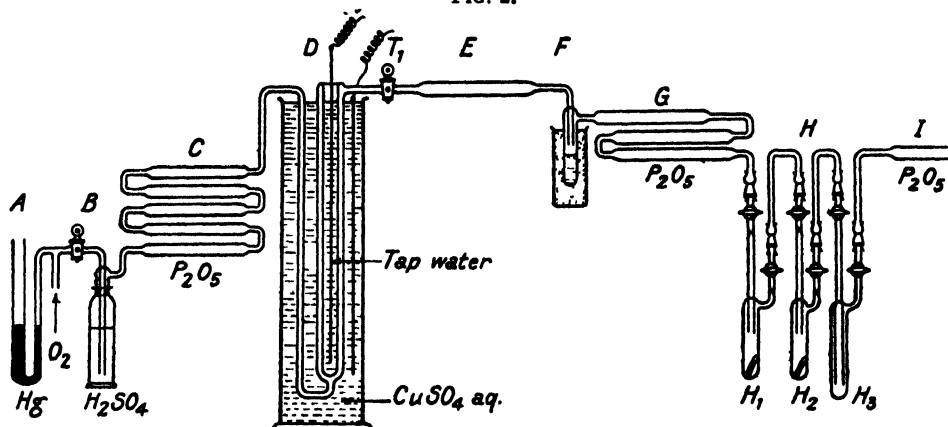
two oxides in solution. Two mixtures containing a trace of moisture are indicated by crosses in Fig. 1, where the f. p.'s are a little below those of the dry series of mixtures. One of these wet mixtures, containing 25·7% N_2O_5, froze at − 3·5°; but, when supercooling of this oxide occurred, the liquid became turbid at − 8·2°, and deposited the tetroxide at − 22°. In both cases it was noticed that the completely frozen mixtures at temperatures a few degrees below the eutectic temperature exhibited a more pronounced light yellow colour than the completely anhydrous mixtures, which were only very pale yellow at these temperatures.

The exact concentrations at which two liquid layers are formed are not yet known; but, since Bousfield (J., 1919, **115**, 45) found that the limit of solubility of nitric acid in nitrogen peroxide at 18° is 8·05% by weight of HNO_3 (or 1·15% H_2O, 6·9% N_2O_5), it is clear that the addition of little more than 1 part of water would suffice to bring about a separation of nitric acid in a mixture of 7 parts of nitric anhydride with 92 parts of nitrogen peroxide. The small proportion of water that is required to produce two liquid layers, especially at low temperatures, is shown by the fact that a sample, which was wet enough to be turbid at − 8·2°, gave a f. p., which was only about 2° below the curve for the dry mixtures.

EXPERIMENTAL.

The apparatus is shown in Fig. 2. All taps and ground joints were lubricated with a little Apiezon L grease, which is comparatively resistant to attack by the substances used. Oxygen

from a cylinder was passed through a sulphuric acid bubbler B, and dried in a series of phosphoric oxide tubes C, before passing through the ozoniser D, 50 cm. in length and cooled by circulating tap-water through the inner tube, in which about 8% ozone was produced by a silent discharge of 500 cycles at 8000—10,000 volts. The ozonised oxygen passed through a tap T_1, and drying tube E, into a receiver F, which had been filled in a vacuum with liquid nitrogen peroxide and sealed on to the ozoniser whilst the nitrogen peroxide was frozen hard. Dry oxygen was passed through the apparatus for 15—20 mins. before the nitrogen peroxide was allowed to melt. The receiver F was then surrounded by a water-bath, the temperature of which was adjusted to control the rate of evaporation of the liquid and to eliminate the heat of reaction of nitrogen peroxide and ozone; injection of the vapour of nitrogen peroxide into a stream of ozone was abandoned, on account of difficulty of control. The vapour was decolorised by the ozone, and, after passing through the drying-tubes G, was condensed in three receivers H_1, H_2, H_3, cooled with solid carbon dioxide and acetone. These were fitted with taps and interchangeable ground joints, so that they could be connected together or transferred to an apparatus from which known weights of nitrogen peroxide could be condensed in them. The first two, about 1 cm. in diameter, were weighed and used to condense quantities up to 2 g. of nitric anhydride, from which two mixtures with the tetroxide could then be made. The third receiver, which was larger and had a longer and wider inner tube, served to condense the residual pentoxide, which was afterwards transferred to one of the smaller receivers. Blocking of these receivers with solid pentoxide was provided for by a " blow-off " A at the other end of the apparatus. The residual gas, after passing through a drying tube I, was heated to decompose the excess of ozone, and bubbled through aqueous caustic soda to remove nitrogen peroxide.

The rate of evaporation of nitrogen peroxide was regulated so that it was completely decolorised; if the condensed pentoxide still contained by chance a trace of peroxide, this was removed by allowing the receiver to warm to room temperature, with the tap leading to the pump line closed, and momentarily opening the tap as many times as was necessary to remove the whole of the brown peroxide from the vapour. The exhausted receivers were allowed to warm to room temperature for weighing, and then cooled again as quickly as possible. The product was a white crystalline powder, which became yellow and wet when allowed to decompose.

SUMMARY.

Nitrogen peroxide and nitric anhydride give a simple freezing-point diagram, with a eutectic at 10·8% N_2O_5 and $-15·8°$.

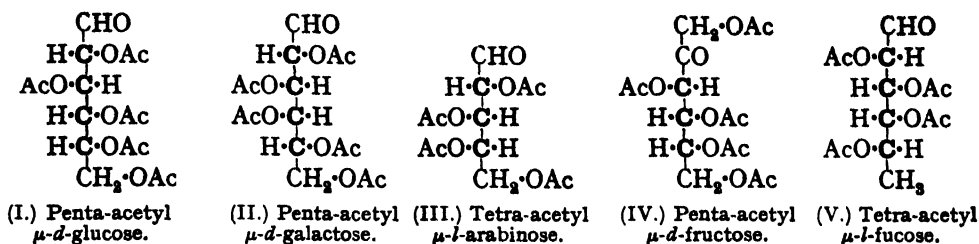**155.** *The Rotatory Dispersion of Organic Compounds. Part XXV. Open-chain Derivatives of Arabinose, Fructose, and Fucose. Optical Cancellation in Penta-acetyl μ-Fructose.*

By W. C. G. BALDWIN, M. L. WOLFROM, and T. M. LOWRY.

IN Part XXIII (J., 1933, 1179) it was shown that, although the asymmetric carbon atoms of penta-acetyl μ-glucose and penta-acetyl μ-galactose, (I) and (II), contribute a *positive* high-frequency term to the rotatory power of these compounds, the corresponding term in tetra-acetyl μ-arabinose (III) vanishes. The whole of the rotatory power of this compound therefore appears to be due to the " induced dissymmetry " of the aldehydic group. In the present paper, the same phenomenon is shown to occur in penta-acetyl μ-fructose (IV) (Wolfrom and Thompson, *J. Amer. Chem. Soc.*, 1934, **56**, 880), a compound in which the three asymmetric carbon atoms are enantiomorphously related to those of the arabinose acetate, but are linked to the radical $CH_2 \cdot O \cdot CO \cdot CH_3$ instead of to a hydrogen atom. Data are also given for tetra-acetyl μ-fucose (V) (Wolfrom and Orsino, *ibid.*, p. 985), which behaves in much the same way as penta-acetyl μ-galactose (II), the four asymmetric carbon atoms of which are enantiomorphously related to its own, but are linked (at the opposite end from the aldehydic group) to methyl instead of to the radical $CH_2 \cdot O \cdot CO \cdot CH_3$. A

number of open-chain derivatives of arabinose and fructose were also examined. These could only be studied in the region of transparency, in which the rotatory dispersion appeared to be simple; but definite evidence was obtained that the process of optical cancellation does not extend to this series of derivatives.

| CHO | CHO | | CH₂·OAc | CHO |

```
      CHO              CHO                              CH₂·OAc            CHO
    H·C·OAc          H·C·OAc            CHO               CO            AcO·C·H
   AcO·C·H          AcO·C·H          H·C·OAc           AcO·C·H          H·C·OAc
    H·C·OAc         AcO·C·H          AcO·C·H            H·C·OAc         H·C·OAc
    H·C·OAc          H·C·OAc         AcO·C·H            H·C·OAc         AcO·C·H
   CH₂·OAc          CH₂·OAc          CH₂·OAc           CH₂·OAc           CH₃
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(I.) Penta-acetyl μ-d-glucose.   (II.) Penta-acetyl μ-d-galactose.   (III.) Tetra-acetyl μ-l-arabinose.   (IV.) Penta-acetyl μ-d-fructose.   (V.) Tetra-acetyl μ-l-fucose.

Arabinose and Fructose.—Optical cancellation implies that, when allowance has been made for the low-frequency partial rotations of an optically active absorption band, the residual high-frequency rotations are negligible. Thus, in the case of tetra-acetyl μ-arabinose, the difference curve (obtained by subtracting the calculated partial rotations of the aldehydic group from the observed total rotations of the acetate) cuts the axis of wavelengths in four points; and the areas of the loops on either side of the axis are so nearly equal that no definite positive or negative sign can be attributed to the residual high-frequency rotation. The cancellation of the partial rotations of the asymmetric carbon atoms in this compound is, however, accompanied by an equality in magnitude of the negative and positive maxima which is more precise than the theoretical dispersion equations would lead us to expect. In particular, Kuhn and Braun's formula forecasts a difference of 200° between the magnitudes of the positive and the negative maximum associated with the aldehydic absorption band, whilst Lowry and Hudson's formula forecasts a difference of 30°. The latter difference is, however, of the same order of magnitude as the unsmoothed ripples on the curve of residual rotations. It is therefore at present impossible to say whether the two maxima, on the curve which represents the isolated partial rotations of the aldehydic radical, (i) should be exactly equal in magnitude, as experiment appears to indicate, or (ii) should differ by about 2%, as the second dispersion formula suggests. Since, however, this formula is admitted to be only a further approximation towards the ideal, we prefer to regard the equality of the negative and the positive maximum as a valid rough-and-ready test of optical concellation, and to ignore the small inequalities predicted by our present imperfect formula.

TABLE I.

Maximum Specific Rotations of Open-chain Acetates.

	First maximum	Reversal.	Second maximum.
I.	− 464° at 3113 A.U.	2969 Å.U.	+ 755° at 2600 Å.U.
II.	−1090 ,, 3113 ,,	2925 ,,	+1420 ,, 2650 ,,
III.	−1145 ,, 3122 ,,	2909 ,,	+1145 ,, 2678 ,,
IV.	500 ,, 3020 ,,	2830 ,,	− 500 ,, 2580 ,,
V.	1130 ,, 3150 ,,	2980 ,,	−1755 ,, 2702 ,,

The maxima for the four aldehydes and one ketone which have now been examined are set out in Table I. In accordance with the conclusion reached above, the *equality* of the two maxima, ± 500°, in the rotatory-dispersion curve of penta-acetyl μ-fructose, is once more within the limits of experimental error. The *signs* of the maxima are, however, reversed in the two compounds, since the asymmetric carbon atoms, which are responsible for the induced activity of the aldehydic group, are themselves opposite in sign. As a further point of contrast, the *range* between the two maxima is reduced from 2290° in the aldehyde to 1000° in the ketone, in which the carbonyl group evidently develops a much smaller induced activity. The change from the aldehyde to the ketone is also accompanied by a displacement of the *wave-length* of the maximum of selective absorption from 2900 to 2830 Å.U., of the maximum of circular dichroism from 2910 to 2806 Å.U., and of the reversal of

z z

sign from 2900 to 2830 Å.U. These differences correspond with the change of wave-lengths from $\lambda_0 = 2850$ to 2700 Å.U., which is observed on passing from aldehyde to acetone.

Galactose and Fucose.—An interesting comparison between the aldehydic acetates of galactose and fucose can be made with the help of Table II, in which the partial molecular rotations of the asymmetric carbon atoms and of the aldehydic or ketonic group are set out separately for the yellow sodium line.

TABLE II.

Partial Molecular Rotations, [M]$_D$, of Aldehydic Sugars.

|		I.	II.	III.	IV.	V.
Partial rotation of CO group	=	− 109°	− 238°	− 188°	+ 119°	+ 239·0°
Partial rotation of other groups	=	+ 89	+ 145	[− 9] *	[+ 15] *	− 105·5
Total rotation	=	− 20	− 93	− 197	+ 134	+ 133·5

* The residual rotations −9° and +15° may be attributed to the failure of the theoretical formula to give equal maxima of opposite sign, and should not be regarded as real.

Galactose and fucose have the same configurations as arabinose and fructose as regards the first three asymmetric carbon atoms; but they contain also a *fourth* asymmetric carbon atom, in which the radicals are on the same side as in the first atom. This additional asymmetric carbon atom gives rise directly to a large high-frequency partial rotation, $[M]_D + 145°$, in the galactose acetate, where the fourth asymmetric group is $CH(OAc)\cdot CH_2\cdot OAc$, and $[M]_D − 105°$ in fucose, where it is $CH(OAc)\cdot CH_3$; but this fourth atom is so remote from the aldehydic group that the inactive terminal group ($\cdot CH_2\cdot OAc$ or CH_3), although it has a substantial influence on the rotatory power of the asymmetric carbon atom to which it is attached, does not appear to have any effect at all on the aldehydic group. In these circumstances, the induced activity of this group reaches almost identical maximum values of − 238° in the galactose acetate (II) and + 239° in the fucose acetate (V), the induced activity being, as usual, opposite in sign to the fixed activity of the asymmetric carbon atoms.

FIG. 1.

Absorption and Circular Dichroism of Penta-acetyl µ-Fructose.
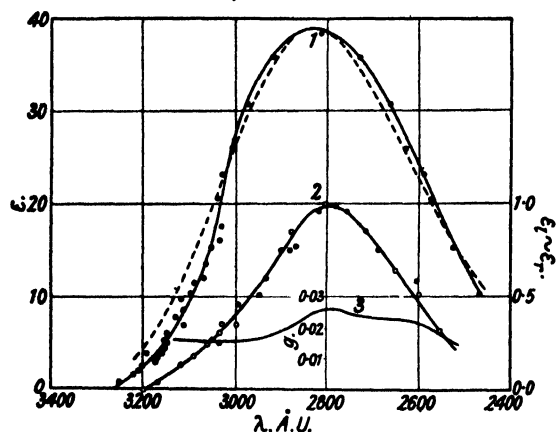
Curve 1. *Molecular extinction coefficients, ε, in chloroform observed (full line) and calculated from Hudson's general equation with n = 2 (broken line).*
„   2. *Circular dichroism, ε$_l$ ~ ε$_r$.*
„   3. *Dissymmetry factor, (ε$_l$ ~ ε$_r$)/ε.*

The elimination of the *fourth* asymmetric carbon atom of galactose or fucose reduces the induced activity of the aldehydic group to $[M]_D − 188°$ in the arabinose acetate (III) ; and the reversal of sign of the *third* asymmetric carbon atom reduces it to $[M]_D − 109°$ in the glucose acetate (I). A similar reduction to $[M]_D + 119°$ occurs when the aldehydic radical of the arabinose acetate is converted into a ketonic radical in the fructose acetate (IV) of opposite sign.

Form of the Absorption Curves.—All the preceding compounds exhibit the characteristic ultra-violet absorption band of the carbonyl group. In the compounds (I) and (II) the absorption curve is symmetrical on a scale of wave-lengths and can be expressed satisfactorily by Lowry and Hudson's equation (Part XXIII, Figs. 1 and 2). The absorption curves (Curve 1, in Figs. 1 and 2) of the open-chain acetates of fructose and fucose, (IV) and (V), however, resemble that of the arabinose acetate, (III), in that they are *steeper on the low-frequency side* (compare *ibid.*, Fig. 3). Hudson (Thesis, Cambridge, 1933, p. 164)

has suggested that curves of this kind might be expressed by a general equation of the type

$$\epsilon = \epsilon_{max.} \, e^{-[(\nu_0/\nu)^n(\nu_0-\nu'/\theta)]^2} \qquad \qquad (1)$$

where ν_0 is the frequency of the maximum and θ is related to the half-width λ' or ν' of the band by $\theta = c\lambda'/1·6651\lambda_0^2$ or $\theta = 1·6651\nu'$. Attempts were therefore made to apply this equation with $n = 2$, but the theoretical curves still sloped less steeply than the experimental curves on the side of longer wave-lengths.
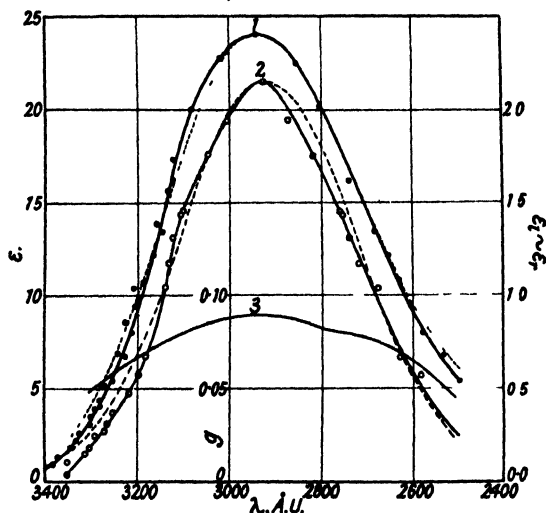
Circular Dichroism.—The circular dichroism of the fructose and fucose acetates is shown as Curve 2 in Figs. 1 and 2. On the assumption that the dissymmetry factor, $(\epsilon_l - \epsilon_r)/\epsilon$, in a given optically active absorption band, is proportional to the frequency, the circular dichroism for $n = 2$ is given by the equation

$$(\epsilon_l - \epsilon_r) = (\epsilon_l - \epsilon_r)_{max.} \, (\lambda_0/\lambda)e^{[(\lambda-\lambda_0)/\theta^2]} \qquad \qquad (2)$$

A curve of this kind agrees rather closely with the experimental data for the fructose acetate (Fig. 1), but the approximation is not so good in the case of the fucose acetate (Fig. 2), where the theoretical curve is represented by a broken line.

Complexity of the Carbonyl Absorption Band.—In a homogeneous absorption band, the maxima of absorption and of circular dichroism should occur at approximately the same wavelength, the half-width of the two curves should be the same, and the ratio $(\epsilon_l \sim \epsilon_r)/\epsilon$ should be proportional to the frequency and should therefore increase slightly on passing through the band in the direction of higher frequencies. The complexity of the ketonic absorption band of camphor was disclosed by the fact that the circular dichroism is concentrated on the low-frequency side of the absorption band; and Lowry and Lishmund (this vol., p. 709) have observed an identical displacement of the maximum in carvomenthone. Table III contains the relevant data for the open-chain acetates (I)—(V).

FIG. 2.

Absorption and Circular Dichroism of Tetra-acetyl μ-Fucose.

Curve 1   Molecular extinction coefficients, ε, in chloroform.
   ,,   2   Circular dichroism, $\epsilon_l \sim \epsilon_r$, with curve calculated from Hudson's general equation $(n - 2)$
   ,,   3.   Dissymmetry factor, $(\epsilon_l \sim \epsilon_r)/\epsilon$

TABLE III.

Absorption and Circular Dichroism of Open-chain Acetates.

|	log ε (max).	Half-width	$(\epsilon_r - \epsilon_l)$ (max)	Half-width
I	1·505 at 2920 Å U.	423 Å U.	1·00 at 2920 Å U.	420 Å U
II.	1·460 ,, 2900 ,,	500 ,,	2·25 ,, 2910 ,,	400 ,,
III	1·580 ,, 2900 ,,	470 ,,	1·80 ,, 2910 ,,	400 ,,
IV.	1·591 ,, 2830 ,,	472 ,,	1·00 ,, 2800 ,,	392 ,,
V.	1·380 ,, 2935 ,,	520 ,,	2·15 ,, 2924 ,,	446 ,,

In every case the two maxima occur at substantially the same wave-length, so that the displacement of the maximum, observed in the cyclic ketones, is not reproduced in the open-chain aldehydes and ketone now under consideration. In general, however, the half-width of the band of circular dichroism is less than that of the absorption band, with the result that the dissymmetry factor, instead of increasing progressively with decreasing wave-length, passes through a maximum near the middle of the absorption band. This effect is least obvious in penta-acetyl μ-glucose, where the same maximum and half-width

were used to calculate the two curves (*loc. cit.*, Fig. 1); conversely, the displacement of the maximum is greatest in the ketone (IV), where it may be as much as 30 Å.U., as compared with 110° in the case of camphor.

The increased width of the absorption band, in comparison with that of the curve of circular dichroism, provides clear evidence of its composite character, and is compatible with the view that the optically active absorption band is accompanied by a wider but weaker
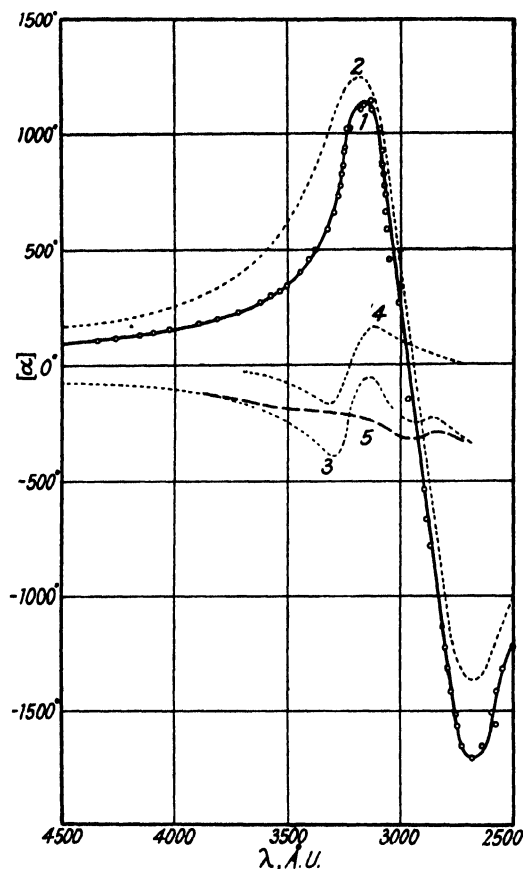
FIG. 3.

Rotatory Dispersion of Penta-acetyl μ-Fructose.

FIG. 4.

. *Rotatory Dispersion of Tetra-acetyl μ-Fucose.*
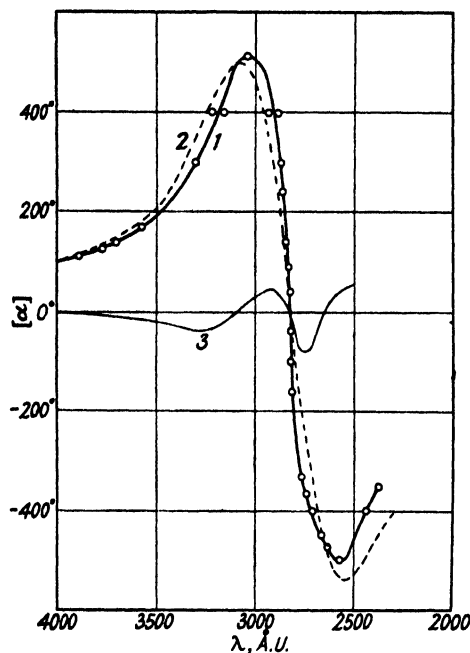
Curve 1. *Observed rotations.*
  „   2. *Partial rotation of carbonyl group.*
  „   3. *Residual rotation (Curve 1 minus Curve 2).*

Curve 1. *Observed rotation.*
  „   2. *Partial rotation of carbonyl group.*
  „   3. *Residual rotation (Curve 1 minus Curve 2).*
  „   4. *Subsidiary partial rotation.*
  „   5. *Residual rotation corrected (Curve 3 minus Curve 4).*

and less active band, with a maximum at the same wave-length. This conclusion has already been considered tentatively as an explanation of the fact that absorption bands which are perfectly symmetrical are often pinched at the top and widened at the bottom, in comparison with the calculated curves; but measurements of circular dichroism provide evidence of complexity which is of a more direct and positive character, so that only the origin of the complexity remains open to question. Thus, as an alternative to the preceding suggestion, the falling off of the dissymmetry factor on the side of shorter wave-lengths might be due to overlapping by an inactive "acetate" absorption band of higher frequency; and a falling off on the side of longer wave-lengths has already been attributed in several cases to

the presence of a small optically active band of opposite sign, in close agreement with parallel observations of rotatory dispersion in the region of absorption.

Form of the Dispersion Curves.—The specific rotations of penta-acetyl μ-fructose and of tetra-acetyl μ-fucose are set out in Tables IV and V and are plotted in Figs. 3 and 4.

TABLE IV.

Rotatory Dispersion of Penta-acetyl μ-Fructose at 20°.

(a) : $c = 8·68$ g./100 c.c.; $l = 2$ dm.; $[α] = 5·764α$.
(b) : $c = 1·7616$ g./100 c.c.; $l = 1$ dm.
(c), (d), (e), (f) : $c = 1·28, 2·056, 1·028, 1·161$ g./100 c.c.; $l = 1$ cm.
All solutions in chloroform (free from alcohol).

$$[α_1] = \frac{9·599}{λ^2 - 0·06792}; \; [α_2] = \frac{7·4367}{λ^2 - 0·078664} + \frac{2·3036}{λ^4}.$$

Visual readings (Soln. a).

λ.	[α].	(O–C) for [α₁].	(O–C) for [α₂].	λ.	[α].	(O–C) for [α₁].	(O–C) for [α₂].	λ.	[α].	(O–C) for [α₁].	(O–C) for [α₂].
Li 6708	25·30°	+0·20°	+0·04°	Ag 5472	41·20°	−0·30°	−0·20°	Zn 4811	58·90°	+0·20°	+0·28°
Cd 6438	27·70	±	±	Hg 5461	41·80	+0·15	+0·18	Cd 4800	59·00	−0·02	±
Zn 6362	27·95	−0·53	−0·53	Cu 5219	46·60	−0·30	−0·25	Zn 4722	61·90	±	±
Li 6104	31·83	+0·36	+0·35	Ag 5209	47·00	−0·15	−0·08	Zn 4680	64·00	+0·50	+0·45
Na 5893	34·30	−0·03	+0·04	Cu 5153	48·50	−0·05	+0·01	Cd 4678	63·10	−0·52	−0·52
Hg 5780	36·00	±	±	Cu 5106	50·00	+0·17	+0·25	Ba 4554	69·35	+0·55	+0·45
Cu 5700	37·20	−0·15	−0·09	Cd 5086	50·35	±	+0·15	Hg 4358	79·30	+0·60	+0·38
Ba 5536	40·35	0·15	+0·18	Ba 4934	54·17	−0·48	−0·40				

Photographic readings (Soln. a).

λ.	[α].	(O–C) for [α₁].	(O–C) for [α₂].	λ.	[α].	(O–C) for [α₁].	(O–C) for [α₂].	λ.	[α].	(O–C) for [α₁].	(O–C) for [α₂].
Fe 4258	84·3	−0·3	−0·9	Fe 3878	119·0	+2·7	+0·1	Fe 3715	142·0	+ 5·1	±
Fe 4185	90·1	+0·6	−0·3	Fe 3821	124·8	+1·9	− 1·5	Fe 3594	165·0	+ 8·6	+0·3
Fe 4107	95·8	+0·5	−0·5	Fe 3794	130·5	+4·2	+0·6	Fe 3556	176·5	+12·4	+2·4
Fe 3983	107·3	+1·5	−0·3	Fe 3742	136·2	+3·2	−1·2	Fe 3521	189·0	+18·0	+6·3
Fe 3925	113·2	+2·0	−0·4								

Region of absorption.

Soln.	λ.	α.	[α].	Soln.	λ.	α.	[α].	Soln.	λ.	α.	[α].
b	3417	3·52°	199·7°	d	3205⎱ 2900⎰	0·82°	400°	c	2788	−0·04°	− 30°
b	3280	5·28	299·6					c	2790	−0·17	−130
c	3230⎱ 2858⎰	0·38	300	c	3018	0·64	500	f	2478⎱ 2772⎰	−0·41	−350
				d	3018	1·03	500				
b	3222	6·82	387·3	e	2850	0·28	270	f	2699⎱ 2507⎰	−0·52	−450
c	3175⎱ 2858⎰	0·51	400	d	2830	0·15	150				
				d	2807	0·09	40	f	2570	−0·58	−500

(*a*) In the region of transparency, the rotatory dispersion of penta-acetyl μ-fructose can be expressed by a single term of Drude's equation as far as 4107 Å.U., but a third constant is needed to extend the range to 3594 Å.U., beyond which a fourth constant appears to be required. In the region of absorption, the partial rotation of the carbonyl group was not calculated from the observed circular dichroism, but with the help of an arbitrary factor, selected to give the closest possible fit to the experimental curve. The curve of residual rotations crosses the axis at four points, the largest ripple being due to the fact that Lowry and Hudson's equation does not give equal positive and negative maxima, like the experimental curve.

(*b*) In the region of transparency, the rotatory dispersion of tetra-acetyl μ-fucose was expressed as far as 3547 Å.U. by means of a Drude equation with three constants. In the region of absorption, the partial rotation of the aldehydic group, calculated from the circular dichroism by means of Lowry and Hudson's equation, leaves a substantial *negative* high-frequency rotation when subtracted from the observed total rotation. The curve of residual rotations, however, again shows a substantial ripple in the neighbourhood of the second (negative) maximum. This ripple can be largely reduced by postulating a small optically active band of opposite sign with a maximum at about 3200 Å.U. The existence of such a band can be justified by the steep fall of the foot of the curve of circular dichroism on the side of longer wave-lengths, and is in agreement with similar conclusions already reached in the case of the glucose acetate (*loc. cit.*, Fig. 4).

TABLE V.

Rotatory Dispersion of Tetra-acetyl μ-Fucose at 20°.

(a), (b), (c) : $c = 2.108, 2.416, 2.380$ g./100 c.c.; $l = 2$ dm.; $[a_s] =$ about 20a.
(d), (e), (f), (g) : $c = 2.380, 1.125, 0.993, 1.039$ g./100 c c.; $l = 1$ cm.; $[a] = 400—1000a$.
(a)—(f) in $C_2H_2Cl_4$; (g) in $CHCl_3$.

$$[a] = \frac{11.7236}{\lambda^2 - 0.09059} - \frac{1.8301}{\lambda^2}.$$

Visual readings.

Soln.	λ	[a]	(O–C)	Soln.	λ	[a].	(O–C)	Soln.	λ.	[a].	(O–C).
b	Li 6708	28.15°	−0.41°	b	Ag 5472	49.70°	−0.19°	b	Cd 5086	62.70°	±
a	Li 6104	36.71	+0.02	b	Hg 5461	50.50	+0.15	b	Ba 4934	69.15	−0.03°
b	Na 5893	40.20	−0.23	b	Cu 5219	57.80	−0.02	b	Zn 4811	76.20	+0.70
ab	Cu 5782	42.62	±	b	Ag 5209	58.00	−0.25	a	Zn 4722	80.35	+0.05
ab	Hg 5780	42.87	+0.20	b	Cu 5153	60.05	−0.10	b	Cd 4678	83.50	+0.41
b	Ba 5536	48.65	+0.22								

Photographic readings.

Soln.	λ	[a]	(O–C)	Soln.	λ	[a]	(O–C)	Soln.	λ	[a]	(O–C)
c	Fe 4325	111.0	−1.9	c	Fe 4031	150.0	−1.8	c	Fe 3631	270.0	−0.1
c	Fe 4271	120.0	+2.1	c	Fe 3900	180.0	+1.4	c	Fe 3547	320.0	+1.2
c	Fe 4163	130.0	−1.3	c	Fe 3821	200.0	+0.7	c	Fe 3513	340.0	−4.0
c	Fe 4103	140.0	±	c	Fe 3727	230.0	+0.2	c	Fe 3454	400.0	+7.0

Region of absorption.

Soln.	[a]	λ	Soln.	[a]	λ	Soln	[a]	λ.
d	450°	3413, 3057	e	1120°	3165, 3125	f	−1080°	2797
d	500	3392, 3057	e	1149	3134	f	−1120	2775
d	580	3330, 3071	e	267	3009	f	−1180	2769
d	660	3298, 3075	e	0	2991	f	−1280	2766
d	730	3280, 3075	e	133	3000	f	−1340	2760
d	770	3275, 3079	e	− 151	2976	f	−1400	2755
d	820	3270, 3083	e	− 285	2970	f	−1500	2750
d	866	3262, 3087	e	− 418	2922	g	+1223	3194, 3150
d	930	3254, 3100	e	− 540	2902	g	−1128	2832, 2510
d	1020	3230, 3100	e	− 668	2898	g	−1225	2820, 2522
d	1100	3180, 3131	e	− 784	2876	g	−1416	2794, 2585
e	819	3265, 3080	f	− 886	2840	g	−1561	2767, 2591
e	916	3257, 3083	f	− 950	2826	g	−1660	2744, 2647
e	1015	3244, 3095	f	−1020	2806	g	−1755	2702

Open-chain Derivatives of Arabinose and Fructose.—The two compounds in which the phenomenon of optical cancellation has been observed are of similar (but opposite) configurations, as regards the three asymmetric carbon atoms which they both contain. Moreover, the first of these atoms is attached in each case to a carbonyl group, and thence to an inactive radical (H or $CH_2 \cdot O \cdot CO \cdot CH_3$), the nature of which does not appear to affect the phenomenon. It was therefore of interest to study the rotatory dispersion of other open-chain derivatives containing three asymmetric carbon atoms of similar orientation, in order to ascertain whether the same phenomenon could be detected in them.
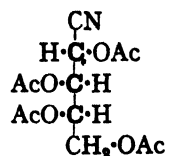
$\overset{\displaystyle CN}{\vert}$	$H \cdot \overset{\vert}{C}(SEt)_2$	$H \cdot \overset{\vert}{C}(SEt)_2$	$AcO \cdot CH_2 \cdot \overset{\vert}{C}(SEt)_2$
$H \cdot \overset{\vert}{C} \cdot OAc$	$H \cdot \overset{\vert}{C} \cdot OH$	$H \cdot \overset{\vert}{C} \cdot OAc$	$AcO \cdot \overset{\vert}{C} \cdot H$
$AcO \cdot \overset{\vert}{C} \cdot H$	$HO \cdot \overset{\vert}{C} \cdot H$	$AcO \cdot \overset{\vert}{C} \cdot H$	$H \cdot \overset{\vert}{C} \cdot OAc$
$AcO \cdot \overset{\vert}{C} \cdot H$	$HO \cdot \overset{\vert}{C} \cdot H$	$AcO \cdot \overset{\vert}{C} \cdot H$	$H \cdot \overset{\vert}{C} \cdot OAc$
$CH_2 \cdot OAc$	$CH_2 \cdot OH$	$CH_2 \cdot OAc$	$CH_2 \cdot OAc$
(VI) Tetra-acetyl *l*-arabono-nitrile	(VII) *l*-Arabinose ethylmercaptal.	(VIII) Tetra-acetyl μ-*l*-arabinose ethylmercaptal.	(IX) Penta-acetyl μ-*d*-fructose ethylmercaptal
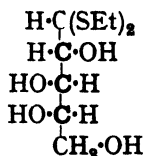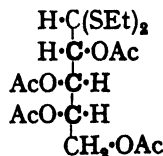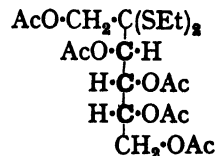
Unlike the five preceding compounds, these four derivatives, (VI)—(IX), exhibit only a general absorption in the accessible ultra-violet region. The absorption bands of the terminal radicals, therefore, lie in a region in which the Cotton effect cannot at present be observed. For this reason, the presence or absence of optical cancellation could not be established by the same direct method as in the two preceding cases, *viz.*, by observations of rotatory dispersion in the region covered by an optically active absorption band.

The rotatory dispersions in the region of transparency are set out in Table VI. These

TABLE VI.

Rotatory Dispersion of Open-chain Derivatives of Arabinose and Fructose at 20°.

) (a) $c = 3.1635$ g./100 c c ; $l = 6$ dm.; (b) $l = 1$ dm.
I) (a) $c = 4.599$ g./100 c.c.; $l = 6$ dm.; (b) $c = 3.369$ g./100 c.c.; $l = 2$ dm.
(VIII) (a) $c = 4.1563$ g./100 c.c.; $l = 6$ dm.; (b) $c = 3.6319$ g./100 c.c.; $l = 1$ dm
(IX) (a) $c = 3.9341$ g./100 c c ; $l = 6$ dm.; (b) $c = 3.0593$ g./100 c.c.; $l = 1$ dm.
(VI), (VIII), (IX) in ethyl acetate; (VII) in formamide.

λ.	Soln. VI (a). [α] = 5.268a. [α].	(O–C).	Soln. VII (a). [α] = 3.623a. [α].	(O–C).	Soln VIII (a). [α] = 4.010a. [α].	(O–C).	Soln. IX (a). [α] = 4.237a. [α].	(O–C).
Cd 6438	3.972°	−0.02°	− 4.71°	+0.02°	−16.48°	−0.13°	12.71°	−0.13°
Na 5893	4.952	+0.12	− 5.66	+0.23	−20.21	−0.11	15.67	±
Hg 5780	5.110	+0.08	− 6.17	+0.02	−21.26	−0.21	16.56	+0.17
Ag 5468	—	—	− 7.18	−0.03	—	—	—	—
Hg 5461	5.690	±	− 6.96	+0.21	−24.26	+0.06	18.80	+0.10
Ag 5209	6.006	−0.29	− 8.12	+0.04	—	—	—	—
Cd 5086	6.480	−0.16	− 8.66	+0.04	−28.71	+0.11	21.85	−0.25
Cd 4800	7.271	−0.29	−10.27	+0.08	−33.69	−0.19	25.07	−0.35
Cd 4678	7.692	−0.32	—	—	−35.49	+0.34	26.90	−0.19
Hg 4358	9.588	+0.18	−13.49	+0.35	−43.27	+0.23	32.35	−0.05

Photographic readings.

Soln.	λ.	[α].	(O–C).	Soln.	λ.	[α]	(O–C).	Soln	λ.	[α].	(O–C).
VI (a)	4230	10.05°	−0.02°	VIII (a)	4360	− 43.30°	+0.10°	VIII (b)	2901	−202.3°	− 3.0°
,,	4096	10.85	±	,,	4176	− 49.32	−0.20	,,	2872	−217.5	− 6.2
,,	4000	11.51	+0.01	,,	4029	− 54.13	+0.52	,,	2868	−217.5	− 4.1
,,	3821	12.95	+0.14	,,	3886	− 60.55	+0.55	,,	2843	−228.5	− 3.9
,,	3631	14.50	±	,,	3720	− 69.37	+0.8	IX (a)	4335	32.32	− 0.53
VI (b)	3576	15.16	+0.15	VIII (b)	4434	− 41.3	+0.2	,,	4213	35.70	+ 0.30
,,	3350	17.72	−0.03	,,	4045	− 53.7	+0.3	,,	4137	37.83	+ 0.69
,,	3203	19.95	+0.05	,,	3764	− 68.8	−1.2	,,	3990	40.78	− 0.21
VII (b)	4680	−10.98	+0.11	,,	3694	− 72.9	−0.3	,,	3930	43.20	+ 0.45
VII (a)	4396	−13.57	+0.09	,,	3581	− 79.9	+0.1	,,	3780	47.43	− 0.10
,,	4260	−15.00	−0.09	,,	3513	− 86.7	−1.1	,,	3714	50.11	±
,,	4144	−16.46	−0.05	,,	3426	− 93.6	+0.1	,,	3605	54.85	+ 0.23
,,	4031	−17.91	+0.19	,,	3339	−103.2	+0.4	,,	3530	58.03	− 0.27
,,	3939	−19.37	+0.35	,,	3271	−111.5	+0.9	IX (b)	3650	50.0	− 2.7
VII (b)	3792	−22.85	+0.07	,,	3108	−140.4	−0.1	,,	3346	68.7	− 0.2
,,	3541	−28.77	+2.27	,,	3047	−154.2	±	,,	3040	101.2	+ 5.2
				,,	2992	−169.3	−0.5	,,	2912	134.0	+20.8
				,,	2929	−188.6	+0.3	,,	2836	161.8	+35.3

are approximately simple, since the specific rotations could be expressed in each case by a single term of Drude's equation, as follows :

$$[\alpha] = \begin{array}{c|c|c|c} \text{(VI.)} & \text{(VII)} & \text{(VIII.)} & \text{(IX)} \\ \dfrac{+ 1.5577}{\lambda^2 - 0.024415} & \dfrac{- 1.6123}{\lambda^2 - 0.073461} & \dfrac{- 5.8874}{\lambda^2 - 0.054661} & \dfrac{+ 4.7717}{\lambda^2 - 0.042714} \end{array}$$

λ_0, A.U. = 1563 | 2710 | 2338 | 2066

The value $\lambda_0 = 1563$ Å.U. for the nitrile is not far removed from the value $\lambda_0 = 1460$ Å.U. for sucrose (Lowry and Richards, J., 1924, **125**, 2523; Harris, Hirst, and Wood, J., 1932, 2115). This is in harmony with the fact that the absorption bands of the cyanides, as deduced from measurements of refractive dispersion (Lowry and Henderson, *Proc. Roy. Soc.*, 1932, *A*, **136**, 471), appear to lie in the same region of the spectrum as those of the hydroxyl group. It was therefore impossible to break up the total rotation in such a way as to assign a partial rotation to the cyanide radical. On the other hand, the dispersion constants of the three mercaptals are much larger than those of the simple sugars. They thus afford clear evidence of the existence of new partial rotations, which are not present in the sugars themselves; but the inequality of these coefficients makes it impossible to assign the whole of the rotations to the induced activity of the mercaptal group, since this would be expected to have the same characteristic frequency throughout. Hence, we conclude that the rotatory dispersions of some, at least, of these four derivatives are only

pseudo-simple, and that their observed total rotations must consequently include partial rotations due to the asymmetric carbon atoms, as well as to the mercaptal radicals. There is thus quite clear evidence that the optical cancellation observed in the aldehydic acetates of arabinose and fructose does not persist as a general phenomenon in these derivatives of the two sugars, and so it appears probable that the carbonyl group is essential to the balance of opposite partial rotations which leads to this effect in the two aldehydic acetates cited above.

The substances were prepared at the Ohio State University. When used in Cambridge their m. p.'s were found to agree closely with the published values.

The methods used for measurements of absorption, circular dichroism, and rotatory dispersion have already been described, but a novel feature is found in the use of four *barium* lines, *viz.*, λλ 6496·91, 5535·53, 4934·10, and 4554·037, to fill up gaps in the series of lines used previously in spectro-polarimetry.

SUMMARY.

The phenomenon of optical cancellation, already observed in tetra-acetyl μ-arabinose, occurs also in penta-acetyl μ-fructose, where the three asymmetric carbon atoms have the same relative configuration, but are of opposite signs. Other open-chain derivatives of arabinose and fructose, in which there is no carbonyl group attached to the first asymmetric carbon atom, do not show this effect.

156. *The Rotatory Dispersion of Organic Compounds.   Part XXVI. Acetoin.*
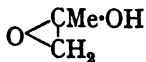
By T. M. LOWRY and W. C. G. BALDWIN.

ACETYLMETHYLCARBINOL, or acetoin (Bouveault and Locquin, *Bull. Soc. chim.*, 1906, **35**, 629), $CH_3 \cdot CH(OH) \cdot CO \cdot CH_3$, the aliphatic analogue of benzoin, is one of the simplest unsaturated optically active compounds. The racemic form has been known since 1890, when Pechmann and Dahl (*Ber.*, **23**, 2421) obtained it as a reduction product of diacetyl, whereas Vladesco in 1891 (*Bull. Soc. chim.*, **6**, 810) prepared it by chlorinating methyl ethyl ketone and hydrolysing the product. The optically active form was first described in 1904 by Desmots (*Compt. rend.*, **138**, 581; cf. Grimbert, *ibid.*, 1901, **132**, 706; Browne, *J. Amer. Chem. Soc.*, 1906, **28**, 467) as a product of the action of various bacteria on polyhydric alcohols and carbohydrates.

The dynamic isomerism of acetoin was studied in 1905 by Kling (*Compt. rend.*, 1905, **140**, 1457), in comparison with that of acetol (I), which had been shown (i) to yield reduction products (propylene glycol and *iso*propyl alcohol) derivable most readily from the isomeric oxide (II) (*ibid.*, 1902, **135**, 970; *Bull. Soc. chim.*, 1903, **29**, 92), (ii) to exhibit in aqueous solutions the behaviour of a pseudo-acid (*Compt. rend.*, 1905, **140**, 1256; *Bull. Soc. chim.*, 1905, **33**, 755), although (iii) the refraction and magnetic rotation of the anhydrous liquid agreed with the ketonic formula. From measurements of refraction, Kling concluded that the monomeric liquid form of acetoin (obtained by distillation of the solid polymeride) was an equilibrium mixture of the ketone (III) with the oxide (IV).

$$CH_3 \cdot CO \cdot CH_2 \cdot OH \qquad O{<}^{CMe \cdot OH}_{CH_2} \qquad CH_3 \cdot CO \cdot CH(OH) \cdot CH_3 \qquad O{<}^{CMe \cdot OH}_{CHMe}$$
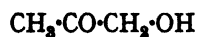
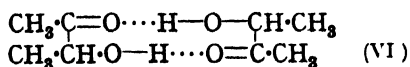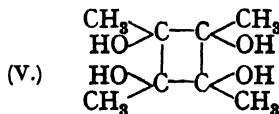(I.)   (II)   (III.)   (IV.)

Pechmann and Dahl (*loc. cit.*) obtained two solid forms, m. p. 126—128° and 94—98°, the former being deposited on long standing, and the latter on freezing in presence of zinc. These were subsequently described by Diels and Stephan (*Ber.*, 1907, **40**, 4336) as melting

at 95·5° and 85·5°. Both forms could be recrystallised from boiling acetone, in which solvent they were shown to be dimeric; but they were depolymerised by contact with ether and could not then be recrystallised. The existence of two forms of the solid was also confirmed by Dirscherl and Braun (*Ber.*, 1930, **63**, 416), who found that they melted at 95° and 85° when heated very slowly, but at 125° and 95° (compare Pechmann and Dahl) when heated rapidly.

Acetoin was recently described by Professor A. J. Kluyver (" Symposium on Bread and Milk," *J. Soc. Chem. Ind.*, 1933, **52**, 373τ) as a precursor of diacetyl in butter. Through his kind introduction, we obtained three specimens from the " N. V. Nederlandsche Gist en Spiritusfabriek " of Delft. The following details of the preparation were supplied by the firm : " A mash containing carbohydrates, nitrogen, and phosphorus compounds was treated with a certain strain of bacteria. These bacteria are capable of partly transforming the carbohydrates into 2 : 3-butylene glycol, $CH_3 \cdot CH(OH) \cdot CH(OH) \cdot CH_3$. When, however, the fermenting liquor is aerated, acetylmethylcarbinol is produced. The substance obtained in this way is lævorotatory, but soon polymerises to the solid, which is the commercial product." Two of the specimens were pale yellow, crystalline solids; the other was a yellow liquid, from which some crystalline material had separated. The yellow liquid was lævorotatory, but both samples of solid were inactive.

Properties of the Solid.—The samples of inactive solid were identical with that which had separated from the active liquid. Thus, the inactive solid, when washed three times with alcohol and dried, melted at 101—102° when heated in the ordinary way, but at 126° when heated rapidly from 115°. The same m. p. was given by the inactive solid deposited from the optically active liquid, after it had been recrystallised quickly from ethyl acetate. When, however, a small quantity of this solid was left over-night in contact with the mother-liquor (ethyl acetate or acetone and chloroform) from which it had separated, it redissolved in the " saturated " solution, owing to depolymerisation. Similarly, an almost unlimited quantity of the solid could be dissolved in warm water, but none was deposited on cooling.

Freezing-point determinations of dilute aqueous solutions of the solid gave a normal molecular weight, $M = 90$ ($C_4H_8O_2 = 88$); but higher values were obtained by determinations of boiling point in non-aqueous solvents, *e.g.*, chloroform, $M = 134$; acetone, $M = 143$; freezing-point determinations in acetic acid gave an intermediate value, $M = 112$. It is therefore clear, in agreement with Diels and Stephan (*Ber.*, 1907, **40**, 4338), that the solid is a dimeric compound, which readily depolymerises on distillation or on dissolution in water. Since, however, solutions prepared by gently warming the solid with ethyl acetate gave *no trace of selective absorption*, it is clear that this polymeride contains no carbonyl groups. We have therefore formulated it as a derivative of *cyclo*butane (V), comparable with the dimeric form of cinnamic acid.

$$
\begin{array}{ll}
\text{(V.)} &
\begin{array}{c}
CH_3{>}C{-}C{<}CH_3 \\
HO \quad | \quad | \quad OH \\
HO{>}C{-}C{<}OH \\
CH_3 \qquad \quad CH_3
\end{array}
&
\begin{array}{c}
CH_3 \cdot C{=}O \cdots H{-}O{-}CH \cdot CH_3 \\
CH_3 \cdot CH \cdot O{-}H \cdots O{=}C \cdot CH_3
\end{array}
\quad \text{(VI)}
\end{array}
$$

These results are directly opposed to those of Dirscherl and Braun (*loc. cit.*), who found that alcoholic solutions, in which the solids were still dimeric ($M = 170$ falling to 100 in 15 mins.) and from which they could be recovered after some hours, gave the same absorption spectrum, $\varepsilon_{max.} = 17 \cdot 8$ at 2800 Å.U., as the monomeride. They therefore concluded that the molecules were united only by secondary valencies as in (VI); but, since our solutions in ethyl acetate were completely transparent in this region, we conclude that their alcoholic solutions must have been partially depolymerised, and that their argument is therefore invalid.

Properties of the Liquid.—On distillation of the yellowish optically active liquid in air, the first runnings were strongly coloured owing to oxidation to diacetyl, but a sample almost free from yellow colour, and of b. p. 142·7—143·2°/760 mm., was obtained by fractionation in a stream of carbon dioxide.

(i) The *absorption spectrum* was examined in the homogeneous state and in solutions in water, ethyl acetate, and cyclohexane. In each case, the ketonic band at 2750 Å.U. was well developed. The data for the three solutions are plotted in Fig. 1. The curves are not symmetrical on a scale of wave-lengths, but can be expressed by Hudson's general equation (see preceding paper, p. 699). The concordance of the observed extinction coefficients with those calculated from Hudson's equation ($n = 2$) can be seen clearly in the data for the homogeneous compound, which are plotted in Fig. 2, from readings taken with a calibrated cell of thickness 0·10 mm.

It is remarkable that the absorption band of acetoin is strongest in aqueous solutions, whereas that of other carbonyl compounds is weakened by hydration. This affords support to the conclusion of Kling (*loc. cit.*) and of Bergmann and Ludwig (*Annalen*, 1924, **436**, 173), that acetoin is a mixture of the ketonic and the oxidic form, (III) and (IV), and that the equilibrium between them is displaced by the action of water; but this solvent appears to favour the ketonic form, and not the oxidic form, as Kling supposed.
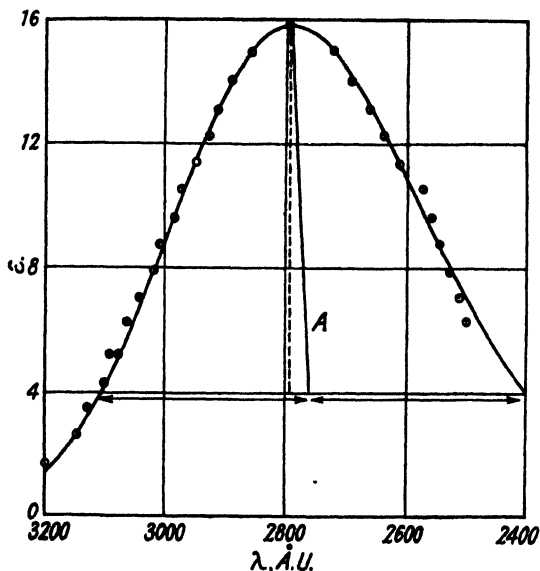
FIG 1.

Absorption Spectra of Acetoin
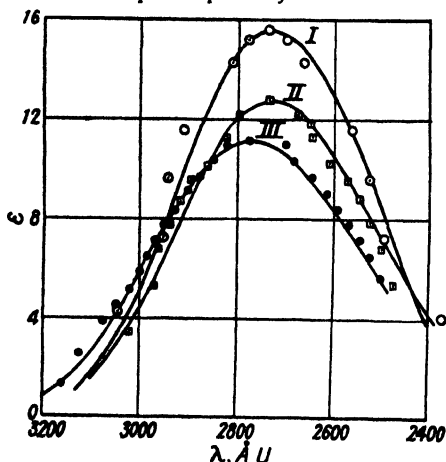
I. *In water.*
II. *In cyclohexane*
III. *In ethyl acetate*
} with calculated curves deduced from Hudson's equation (n = 2)

FIG 2.

Absorption Spectrum of Acetoin (no solvent) with calculated curve deduced from Hudson's equation (n = 2).

The line A *shows the slope of the rectilinear diameter.*

(ii) The *circular dichroism* was too small to be measured, and it was therefore not possible to compare the position of the maximum with that of the maximum of absorption.

(iii) The *rotatory power* of the liquid (d 1·000) was $[\alpha]_{5461} = 6·60°$, but this was increased to 8·04° by fractionation.

(iv) The *rotatory dispersion* of the redistilled liquid (b. p. 142·7—143·2°/760 mm.) was determined without a solvent over the range 6708—3395 Å.U., but could not be followed into the region of absorption. The results are shown in Table I.

Over the whole range of observation the rotations could be expressed by a Drude equation with three constants

$$[\alpha] = -2·1644/(\lambda^2 - 0·084049) + 0·62666/\lambda^2.$$

The dispersion constant of the low-frequency term, $\lambda_0^2 = 0·084049$, $\lambda_0 = 2900$ Å.U., corresponds with the frequency of maximum absorption in the ketonic band, $\lambda_a = 2794$ Å.U. The introduction of a dispersion constant into the high-frequency term was unnecessary at wave-lengths down to about 3600 Å.U., but would be necessary to express the rotations at shorter wave-lengths.

TABLE I.

Specific Rotations of Acetoin at 20°.

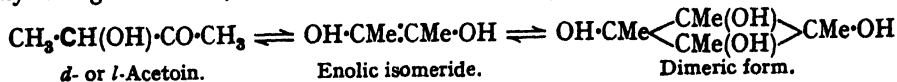No solvent; $l = 2$ dm. except where otherwise noted; $d_4^{20°} = 1\cdot000$; all rotations are negative.

Visual readings.			Photographic readings.		
λ.	[α].	O–C.	λ.	[α].	O–C.
Li 6708	4·47°	0·06°	Fe 5002	10·67°	−0·17°
Ba 6497	4·95	−0·04	Fe 4590	13·95 †	0·18
Cd 6438	5·07	−0·03	Fe 4500	14·95 †	0·22
Li 6104	5·87	−0·05	Fe 4432	15·95 †	0·11
Na 5893	6·42	−0·01	Fe 4368	17·14 *	−0·14
Cu 5782	6·77	±0	Fe 4320	18·20 *	−0·46
Hg 5780	6·76	0·01	Fe 4310	17·95 †	−0·05
Cu 5700	7·07	−0·02	Fe 4266	19·25 *	−0·60
Ba 5536	7·62	0·07	Fe 4178	20·31 *	±0
Ag 5468	7·97	−0·01	Fe 4144	21·39 *	−0·36
Hg 5461	8·04	−0·04	Fe 4101	22·42 *	−0·44
Cu 5219	9·16	0·03	Fe 4060	22·95 †	0·05
Ag 5209	9·12	0·12	Fe 3968	25·45 †	0·07
Cu 5153	9·62	−0·07	Fe 3928	27·20 *	−0·46
Cu 5106	9·86	−0·02	Fe 3872	27·95 †	0·67
Cd 5086	9·97	0·01	Fe 3839	30·29 *	−0·38
Ba 4934	10·93	0·07	Fe 3738	34·40 *	±0
Zn 4811	11·98	−0·01	Fe 3653	38·52 *	0·58
Cd 4800	12·22	−0·15	Fe 3585	42·70 *	0·92
Zn 4722	12·77	0·01	Fe 3521	47·00 *	2·04
Zn 4680	13·20	−0·02	Fe 3478	51·10 *	2·22
Cd 4678	13·14	0·05	Fe 3395	57·33 *	6·62
Li 4602	13·89	0·09			
Ba 4554	14·52	−0·01			
Hg 4358	17·60 *	−0·49			

* $l = 0\cdot4725$ dm. † $l = 1$ dm.

The activity of the compound is due mainly to the low-frequency lævorotation of the carbonyl group, which is about 5 times as great as the high-frequency dextrorotation of the asymmetric carbon atom.

Racemisation of Acetoin.—The specific rotatory power of acetoin is increased by fractional distillation. Its optical activity is therefore resistant to the effects of vaporisation. On the other hand, at the end of a day, the liquid had deposited a considerable proportion of the inactive solid polymeride, from which the inactive monomeride could be prepared by distillation. The rotatory power of the liquid remained very nearly constant during the process of racemisation, as would be expected if the liquid were saturated with the inactive polymeride, so that its concentration in the saturated solution remained constant.

The preceding observations suggest that the racemisation of acetoin is dependent on *reversible polymerisation* rather than on the more usual process of *reversible isomeric change.* It is, however, quite possible that an enolic isomeride is first produced, *e.g.*, by alkaline catalysis in glass vessels, but is converted immediately into the polymeride :

$$CH_3\cdot CH(OH)\cdot CO\cdot CH_3 \rightleftharpoons OH\cdot CMe\raisebox{0pt}{:}CMe\cdot OH \rightleftharpoons OH\cdot CMe\!\!\big<\!\!\begin{smallmatrix}CMe(OH)\\CMe(OH)\end{smallmatrix}\!\!\big>\!\!CMe\cdot OH$$

d- or *l*-Acetoin.   Enolic isomeride.   Dimeric form.

The fact that the formation of the dimeric form is accompanied by a complete loss of optical activity is in harmony with the formula (V), but is not explained by Dirscherl and Braun's formula (VI).

Acetylation of the Solid.—After observations of absorption had shown that the dimeric form of acetoin did not contain any carbonyl groups, an attempt was made to establish the presence of four hydroxyl groups. The solid was therefore acetylated with pyridine and acetic anhydride (Bergmann and Ludwig, *Annalen,* 1924, **436**, 173). The product was identical in odour, in b. p. (168—171°), and in composition (Found : OAc, 45·7. Calc. for $C_6H_{10}O_3$: OAc, 45·4%) with the acetate which they obtained from the monomeride, so acetylation had evidently been accompanied by depolymerisation. The absorption curve of the monomeride is reproduced in Fig. 3. The maximum extinction coefficient of the ketonic absorption band is about 30% stronger than in acetoin, but is

supplemented by a much stronger absorption, rising towards an unreached maximum on the edge of the Schumann region, which can be attributed to the acetate radical.

Acetylation of the Liquid.—The optically active liquid was dissolved in acetic anhydride (11·90 g./100 c.c.). It gave an initial specific rotation, $[\alpha]_D - 12\cdot10°$, about twice as large as that of the pure liquid. This rose during about 3 hours at 18—19°, then fell according to a linear law during the period 91—200 hours, and then more slowly to a negligible value after 578 hours :

t, hrs. ...	0	$\frac{1}{2}$	1	$2\frac{1}{4}$	$19\frac{1}{4}$	72	91	115	145
$[\alpha]_D$	12·10°	12·35°	12·44°	12·60°	11·68°	10·60°	10·41°	9·58°	8·99°
t, hrs. ...	190	235	262	290	331	402	451	477	578
$[\alpha]_D$	7·48°	6·21°	5·37°	4·54°	3·70°	2·52°	1·68°	1·18°	0·17° ($a = 0·02°$)

These changes of rotatory power are attributed to a rapid initial acetylation of the active ketol, followed by a slower racemisation of the acetate; but the mutarotation curve is

FIG. 3.

Absorption Spectrum of Acetoin Acetate.
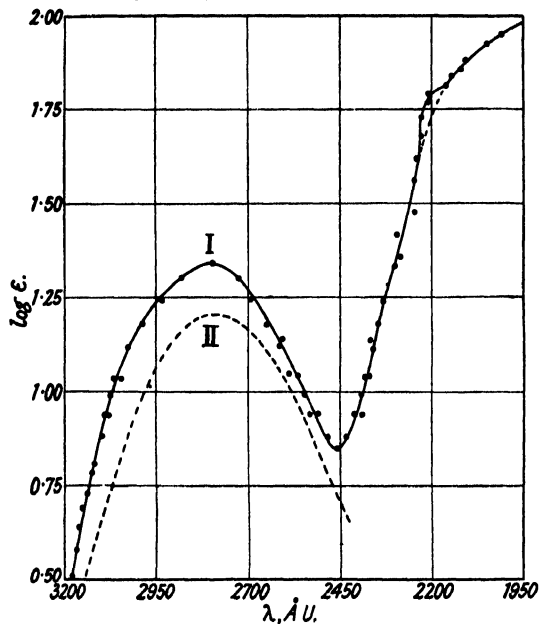
I. *Acetate in* cyclo*hexane (logarithmic scale).*
II. *Acetoin (no solvent) on same logarithmic scale.*

too complex to be readily analysed, and we are unable to express an opinion as to the mechanism of the racemisation.

SUMMARY.

1. Acetoin, or acetylmethylcarbinol, exists as an optically active liquid, $[\alpha]_{5461} = - 6\cdot6°$, from which an optically inactive solid polymeride separates slowly without altering the rotatory power of the saturated solution. The rotatory power can, however, be increased to $[\alpha]_{5461} = - 8\cdot0°$ by fractional distillation.

2. The liquid shows a well-developed ketonic band, but this is absent from freshly prepared solutions of the polymeride.

3. Acetylation of the polymeride yields a monomeric acetate, in which the ketonic band is again fully developed.

157. *The Rotatory Dispersion of Organic Compounds. Part XXVII.*
Menthone and Carvomenthone.

By T. M. LOWRY and R. E. LISHMUND.

MENTHONE (I) and carvomenthone (II), purified in Prof. Read's laboratory at St. Andrews, were investigated in order to ascertain whether they would exhibit the same anomaly as camphor (Kuhn and Gore, *Z. physikal. Chem.*, 1931, *B*, **12**, 389) and camphor-β-sulphonic acid (Lowry and French, *J.*, 1932, 2654), *viz.*, a circular dichroism limited to the long-wave-length side of the ketonic absorption band, which was thus shown to be unexpectedly composite.

(I.) *l*-Menthone. (II.) *l*-Carvomenthone.
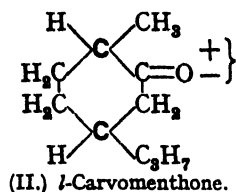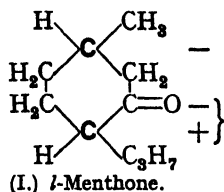
Since the two ketones are both liquid, they cannot be purified as rigorously as camphor; hence, the *l*-menthone may contain a little *d-iso*menthone and a trace of menthol, and the carvomenthone may contain the *cis*- as well as the *trans*-ketone. There is, however, no reason to think that these impurities would have any marked effect on the general course of the anomalies of rotatory dispersion in the region of absorption. We therefore regard as trustworthy the conclusion that the maximum of circular dichroism of carvomenthone is displaced in the same direction as in camphor and to almost exactly the same extent, *viz.*, 110 Å.U. in the direction of longer wave-lengths.

Measurements of the rotatory dispersion of each ketone were carried right through the absorption band, and the complete loop of anomalous rotatory dispersion was plotted. The induced rotation of the ketonic radical of carvomenthone is, as is usual, opposite in sign to the fixed rotation of the asymmetric carbon atoms; but it is noteworthy that the partial rotation of the ketonic band of menthone is of the same sign as the residual rotation. Since we are still entitled to expect that the induced activity of the ketonic radical will be of opposite sign to that of the asymmetric carbon atom to which it owes its activity, this effect may be attributed (as in the α-halogeno-derivatives of camphor, *J.*, 1925, **127**, 1264) to a high-frequency rotation of opposite sign, associated with another (and in this case a more remote) asymmetric carbon atom. If this attribution is accepted, the signs of the different radicals are as indicated alongside the preceding formulæ. It will be seen that opposite signs are attributed to the asymmetric carbon atoms in menthone and in carvomenthone; but this does not necessarily imply a reversal of configuration, since this effect might easily result from the handing over of the carbonyl radical from one asymmetric carbon atom to the other.

Absorption Spectra.—The molecular extinction coefficients in alcohol and in *cyclo*hexane are plotted in Figs. 1 and 2, and the principal constants of the curves are shown in Table I.

TABLE I.

Absorption Spectra of Menthone and Carvomenthone.

Compound.	Solvent.	Maximum.		Width,	Strength,
		ϵ.	λ_0.	λ'.	$f \times 10^4$.
Menthone	EtOH	23·8	2867	443	8·3
,,	C_6H_{12}	20·3	2920	448	7·2
Carvomenthone (sample *a*)	EtOH	22·3	2841	351	6·2
,, (,, *b*)	,,	22·3	2840	360	—
,, (,, *b*)	C_6H_{12}	19·5	2886	454	7·1

The absorption spectra of the two isomerides, in spite of their similarity of structure, show definite points of contrast, since the maximum extinction coefficient, and the strength, *f*

(which depends on the total area of the band), are slightly greater for menthone than for carvomenthone. This difference, however, is less than that produced by changes of solvent. Thus, the alcoholic solutions are more absorbent by about $\frac{1}{4}$ than those in *cyclo*hexane, in spite of the fact that the formation of an alcoholate would tend to eliminate the ketonic absorption band.

The curve for carvomenthone in alcohol is remarkable for the complete absence of general absorption at wave-lengths down to 2540 Å.U. This feature is due to the exceptional optical purity of sample (a) ; but, since the sample (b) used for the measurements of rotatory dispersion ($\alpha_D - 11.20$, $n = 1.4552$) gave the same wave-length and intensity of maximum absorption, and the same half-width (so that the two absorption bands were

Fig. 1.

Molecular extinction coefficients of menthone.
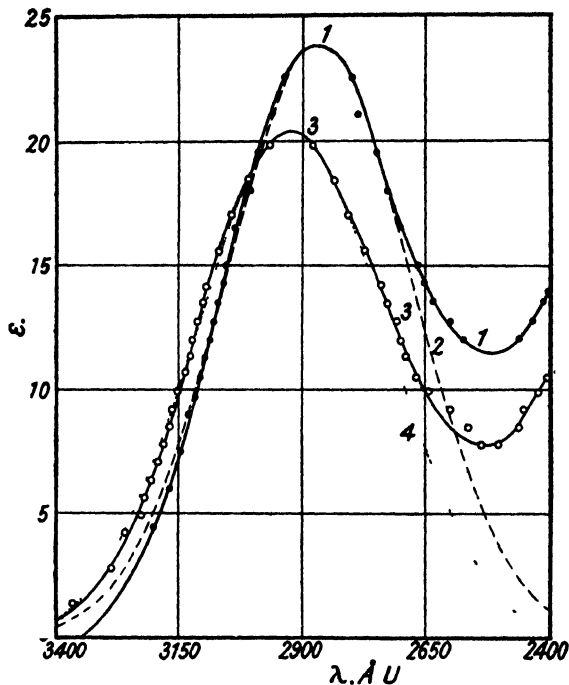
1. In alcohol (obs.).
2. „　　„　　(calc. from Lowry and Hudson's equation).
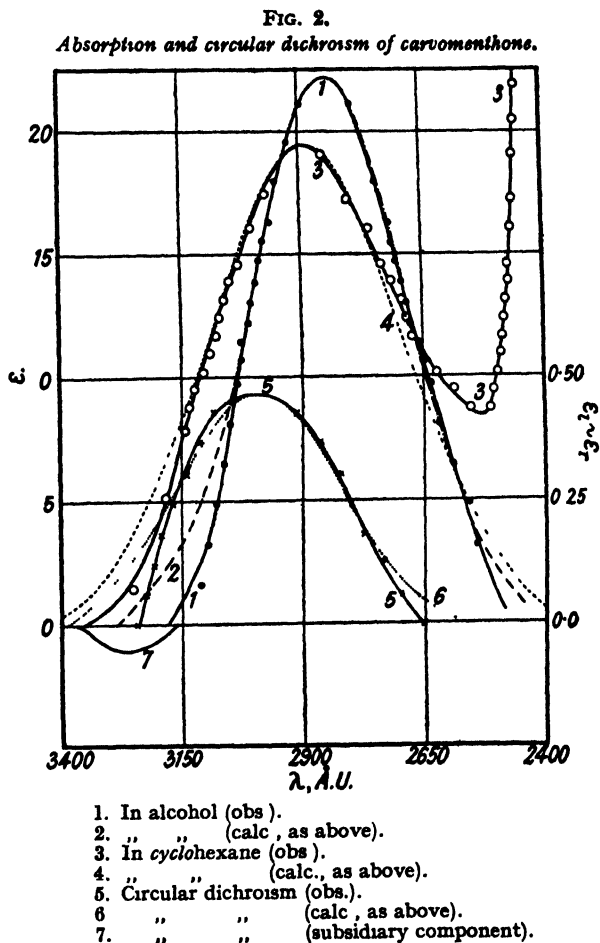3. In *cyclo*hexane (obs).
4. „　　„　　(calc., as above).

identical up to and a little beyond the maximum), we think it unlikely that the unknown impurity, to which the general absorption of sample (b) must be attributed, would affect the curve of anomalous rotatory dispersion in the region covered by the absorption band.

The absorption curve for the alcoholic solution of carvomenthone which showed no general absorption is very nearly symmetrical on a scale of wave-lengths, like those of the xanthates studied by Lowry and Hudson (*Phil. Trans.*, 1933, *A*, **232**, 117), and can be expressed to a close approximation by the equation $\varepsilon = \varepsilon_{max.} e^{-(\lambda - \lambda_0)^2/\theta}$ ($\theta = \lambda'/1.6651$) which they devised to express the form of absorption curves of this type. The same equation was used to calculate the theoretical values for the other three curves; but, since only one arm was fully developed, in consequence of overlapping by the general absorption on the side of shorter wave-lengths, the symmetry of the curves was not so well established.

Circular Dichroism.—The circular dichroism of menthone was too small for accurate measurement, but the values for solutions of carvomenthone in *cyclo*hexane are included in

Fig. 2. The maximum of circular dichroism at 2995 Å.U. is displaced by about 110 Å.U. from the maximum of absorption at 2886 Å.U., exactly as in the case of camphor, where it is displaced from 3020 to 2910 Å.U.

The theoretical curve was calculated by means of Lowry and Hudson's equation (*loc. cit.*), the following parameters being used : $\lambda_0 = 2995$ Å.U.; $(\epsilon_l \sim \epsilon_r)_{max.} = 0.4675$; $\lambda' = 382.1$ Å.U.; $\theta = 229.5$ Å.U. The agreement is good on the side of shorter wavelengths, but the experimental data fall off much more rapidly on the side of longer wavelengths. This anomaly can be attributed to a weak circular dichroism of opposite sign, *e.g.*, $\lambda_{max.} = 3260$ Å.U.; $(\epsilon_l \sim \epsilon_r)_{max.} = 0.054$; $\lambda' = 125$ Å.U., similar to that postulated

FIG. 2.

Absorption and circular dichroism of carvomenthone.

1. In alcohol (obs).
2. „   „   (calc , as above).
3. In *cyclo*hexane (obs).
4. „   „   (calc., as above).
5. Circular dichroism (obs.).
6.   „   „   (calc , as above).
7.   „   „   (subsidiary component).

by Hudson, Wolfrom, and Lowry in penta-acetyl μ-glucose (J., 1933, 1179) and correlated by them with a subsidiary aldehydic absorption band observed by Schou (*Compt. rend.*, 1926, **182**, 965). A weak band of opposite sign in this position is also required in order to eliminate a loop in the residual curve of rotatory dispersion, after allowing for the partial rotation of the principal band.

Rotatory Dispersion.—The rotatory dispersions of menthone and carvomenthone in the region of absorption are tabulated in Tables II and III and plotted in Figs. 3 and 4, and show the following anomalies :

	Negative maximum.	Reversal.	Positive maximum.
Menthone	$[M] = -242°$ at 3025 Å.U.	None.	$-72°$ at 2712 Å.U.
Carvomenthone	$[M] = -868°$ at 3195 Å.U.	3021 Å.U.	$+1170°$ at 2770 Å.U.

TABLE II.

Anomalous Rotatory Dispersion of Menthone at 20° in cycloHexane.

$c = 0.00788$ g./c.c.; $l = 1$ cm.

a (obs.).	[M].	λ, Å.U.	a (obs.).	[M].	λ, Å.U.	a (obs.).	[M].	λ, Å.U.	a (obs.).	[M].	λ, Å.U.
0·05°	− 78°	3266	0·175°	−230°	3068	0·075°	− 92°	2762	0·2°	−211°	2450
0·075	−108	3220	0·175	−228	2981	0·075	−89·5	2642	0·225	−237·5	2431
0·1	−139	3175	0·15	−197	2944	0·1	−113	2591	0·25	−265	2420
0·125	−169·5	3144	0·125	−164	2878	0·125	−138·5	2537	0·275	−290·5	2399
0·15	−201	3117	0·1	−130	2844	0·15	−163·5	2517	0·3	−323	2379
						0·175	−185	2485	0·35	−364	2333

Fig. 3.
Rotatory dispersion of menthone.
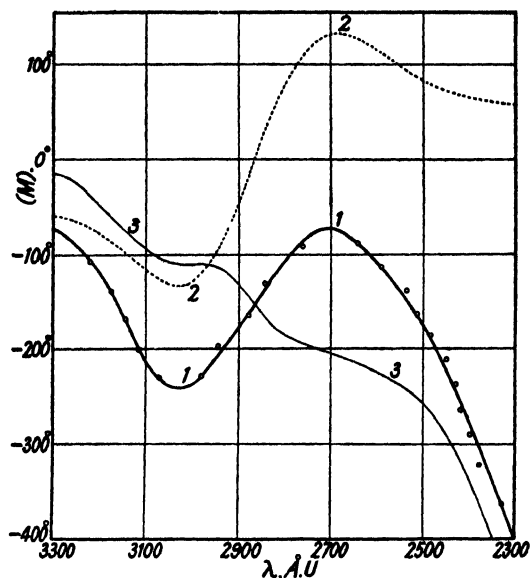
1. Total rotation (obs.).
2. Partial rotation of >CO group (calc.).
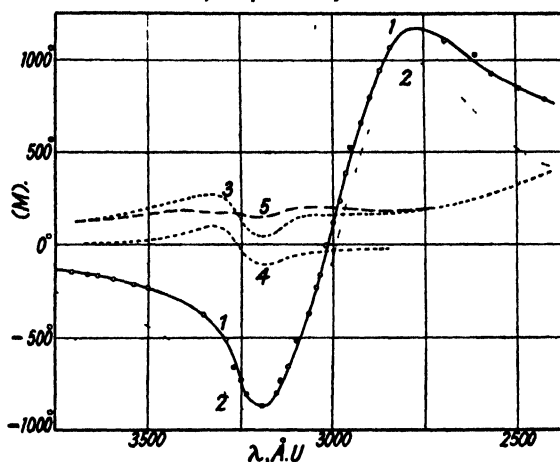3. Residual rotation (Curve 1 minus Curve 2).

TABLE III.

Anomalous Rotatory Dispersion of Carvomenthone at 20° in cycloHexane.

(a) $c = 3.23$ g./100 c.c.; $l = 4$ dm.; (b) $c = 1.081$ g./100 c.c.; $l = 1$ cm.; (c) $c = 0.572$ g./100 c.c. $l = 1$ cm.

(a).			(b).			(c).		
ι (obs.).	[M].	λ, Å.U.	a (obs.).	[M].	λ, Å.U.	a (obs.).	[M].	λ, Å.U.
18°	−208·5°	3541	−0·1°	−156°	3640	0°	0°	3021
15·5	−180	3594	−0·15	−226	3500	0·1	261	2981
13	−150·5	3664	−0·25	−370	3352	0·15	390	2966
12	−139·5	3707	−0·35	−512	3291	0·2	528	2952
10·5	−122	3770	−0·45	−654	3271	0·25	662	2929
9	−104·5	3850	−0·5	−725	3248	0·3	795	2900
8	− 93	3903	−0·55	−796	3235	0·35	940	2873
7	− 82	3982	−0·6	−868	3193	0·4	1070	2843
6·25	− 73	4067	−0·55	−796	3153	0·4	1103	2696
5·5	− 64	4154·5	−0·5	−725	3143	0·35	1030	2612
4	− 47·5	4353	−0·45	−654	3123	0·3	929	2570
3	− 36	4575	−0·35	−512	3100	0·25	850	2492
2	− 24	4940	−0·25	−370	3067	0·2	789	2425
			−0·15	−226	3048			
			−0·1	−156	3037			

It is noteworthy that the curve for menthone, in which the negative anomalous rotation of the carbonyl group is superposed on a negative residual rotation, does not cross the axis, so that the second maximum becomes a minimum. The anomalous partial rotation (calculated from Lowry and Hudson's equation with an arbitrary factor) is exceptionally weak, since the observed range between the two " maxima " is only 170°, as compared with about 2040° for carvomenthone and over 7000° for a solution of camphor in *cyclo*-hexane. On the other hand, the residual rotation is exceptionally large, and rises so steeply (from − 14° at 3300 Å.U. to − 400° at 2350 Å.U.) as to indicate the near approach to a highly active absorption band of shorter wave-length. The ripples on the curve are not of any importance, since they may be due merely to the limitations of the theoretical equation.

FIG. 4.

Rotatory dispersion of carvomenthone.

1. Total rotation (obs.).
2. Partial rotation of >CO group (calc.).
3. Residual rotation (Curve 1 minus Curve 2).
4. Subsidiary partial rotation.
5. Residual rotation corrected (Curve 3 minus Curve 4).

The anomalous partial rotation of the ketonic band in carvomenthone was calculated from the circular dichroism by means of Lowry and Hudson's equation; but the residual partial rotation of high frequency showed a ripple, which was eliminated (as in the case of penta-acetyl μ-glucose) by postulating a subsidiary band of opposite sign, giving rise to a small partial rotation with a reversal of sign at 3260 Å.U.

SUMMARY.

(*a*) The maximum of circular dichroism of carvomenthone is displaced by 110 Å.U. in the direction of longer wave-lengths from the maximum of absorption, exactly as in the case of camphor.

(*b*) Menthone and carvomenthone exhibit anomalous rotatory dispersion in the region of absorption. In the latter, a negative anomalous rotation, with a range of about 2000°, is superposed on a positive residual rotation of high frequency; but in the former, a negative anomalous rotation with a range of less than 200° is superposed on a negative residual rotation, which rises steeply with decreasing wave-length, and is evidently composite in character.
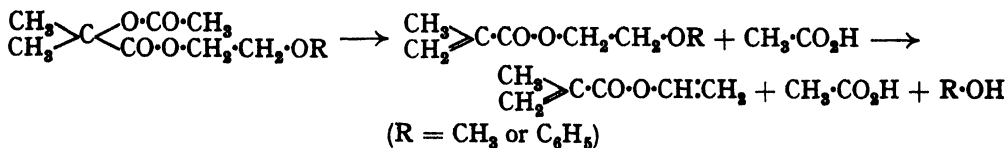
3 A

158. *Studies in Pyrolysis. Part II. The Pyrolysis of Derivatives of α-Acetoxyisobutyric Acid, and Related Substances.*

By ROBERT BURNS, D. TREVOR JONES, and PATRICK D. RITCHIE.

THE new pyrolytic process, applied in Part I (this vol., p. 400) to the synthesis of derivatives of acrylic acid, has now been extended to the synthesis of higher α-substituted homologues of such derivatives.

Methyl α-acetoxyisobutyrate splits up at 490° into acetic acid and methyl α-methylacrylate, the latter being isolated in yields of over 90%, calculated on the acetoxy-ester " cracked."

Aliphatic ethers, in general, pyrolyse into aldehyde and paraffin, though they are fairly thermostable, whereas certain more complex ethers pyrolyse readily into carbinol and olefin (cf. Hurd, " The Pyrolysis of Carbon Compounds," New York, 1929, pp. 198, 228—230). It seemed not impossible, therefore, that under suitable conditions of pyrolysis β-*methoxyethyl* α-*acetoxyisobutyrate* and β-*phenoxyethyl* α-*acetoxyisobutyrate*, owing to the introduction of an ether group, might give rise to vinyl α-methylacrylate, probably in two stages, thus :

$$\underset{CH_3}{\overset{CH_3}{>}}C\underset{CO \cdot O \cdot CH_2 \cdot CH_2 \cdot OR}{\overset{O \cdot CO \cdot CH_3}{<}} \longrightarrow \underset{CH_2}{\overset{CH_3}{>}}C \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot OR + CH_3 \cdot CO_2H \longrightarrow$$

$$\underset{CH_2}{\overset{CH_3}{>}}C \cdot CO \cdot O \cdot CH{:}CH_2 + CH_3 \cdot CO_2H + R \cdot OH$$

$$(R = CH_3 \text{ or } C_6H_5)$$

Only the first stage occurred, however, β-*methoxyethyl* and β-*phenoxyethyl* α-*methylacrylate* respectively being obtained, both in good yield.
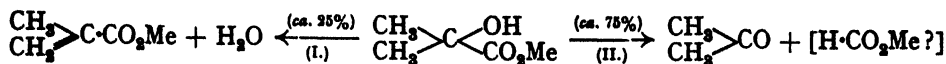
The pyrolysis of acetylated α-hydroxy-nitriles was considered in Part I (*loc. cit.*). In agreement with the general scheme indicated there, it has now been found that acetylated acetone cyanohydrin (α-acetoxyisobutyronitrile) undergoes pyrolysis at 420° in two different ways, the first giving acetic acid and α-methylacrylonitrile in over 90% yield, and the second, which increases in importance as the temperature is raised, yielding small amounts of acetone, hydrogen cyanide, and, presumably, keten.

Acetylation of acetone cyanohydrin by means of acetic anhydride in presence of a little perchloric acid yields approximately equivalent amounts of α-acetoxyisobutyronitrile and N-*acetyl-α-acetoxyisobutyramide* (m. p. 81—82°). The latter compound breaks down as follows, when pyrolysed at 515—530° :

$$\underset{CH_3}{\overset{CH_3}{>}}C\underset{CO \cdot NH \cdot CO \cdot CH_3}{\overset{O \cdot CO \cdot CH_3}{<}} \longrightarrow \underset{CH_2}{\overset{CH_3}{>}}C \cdot CN + 2CH_3 \cdot CO_2H$$
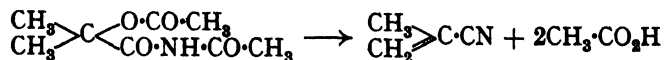
Just as with lactic acid derivatives, the pyrolysis method of indirect dehydration can here be applied in several ways. For instance, in addition to its acetate, the *benzoate* and the chloride of methyl α-hydroxyisobutyrate yield methyl α-methylacrylate at about 500°, by elimination of the appropriate acid, though in the latter case the liberation of hydrogen chloride appears to lead to complications and the yield of methyl methylacrylate is poor.

We have also examined the pyrolysis of acetone cyanohydrin and methyl α-hydroxy-*iso*butyrate in order to determine to what extent, if any, *direct* dehydration occurs at temperatures of 400—600°. The former, as expected, decomposed completely into acetone and hydrogen cyanide, no preferential fission into water and methylacrylonitrile occurring at 510°. Methyl α-hydroxy*iso*butyrate, on the other hand, appeared to split up in two ways at 470—480° :

$$\underset{CH_2}{\overset{CH_3}{>}}C \cdot CO_2Me + H_2O \overset{(ca.\ 25\%)}{\underset{(I.)}{\longleftarrow}} \underset{CH_3}{\overset{CH_3}{>}}C\underset{CO_2Me}{\overset{OH}{<}} \overset{(ca.\ 75\%)}{\underset{(II.)}{\longrightarrow}} \underset{CH_3}{\overset{CH_3}{>}}CO + [H \cdot CO_2Me\,?]$$

About 63% of the hydroxy-ester was recovered unchanged, the remainder undergoing pyrolysis by routes I and II in approximately the ratio shown. Though acetone was identified in the product, the methyl formate (b. p. 32·5°) which would be expected to

accompany it was not observed. It may, perhaps, have undergone secondary pyrolysis into gaseous products (Peytral, *Bull. Soc. chim.*, 1925, 37, 562); and it is at least significant that the total loss of weight in each of three pyrolyses was approximately that calculated for methyl formate from the amount of acetone isolated. Further, no pyrolysis into methyl alcohol and the corresponding cyclic " lactide " was observed.

EXPERIMENTAL.

The apparatus and methods employed were those described in Part I (*loc. cit.*). Where pyrolysis of a solid had to be carried out, the substance was dissolved in acetone (which does not undergo appreciable pyrolysis below 700°), and the solution run into the heated tube as usual.

Methyl α-Acetoxyisobutyrate.—This *ester* was obtained in 84—90% yield by acetylating methyl α-hydroxyisobutyrate with acetyl chloride, or acetic anhydride in presence of a little concentrated sulphuric acid, and fractionating the product. It is a colourless mobile liquid with a pleasant sweetish odour; b. p. 76—77°/18 mm., 78—79°/20 mm., and 169—171°/750 mm., $n_D^{20°}$ 1·413, and $d_4^{20°}$ 1·058 (Found : C, 52·2; H, 7·4. $C_7H_{12}O_4$ requires C, 52·5; H, 7·5%). It is insoluble in water and brine, and soluble in acetone, ether, ethyl alcohol, benzene, and ligroin.

Pyrolysis. 437 G. of the pure ester were run (5·5 c.c./min.) into the vertical pyrolysis tube, maintained at 480—500°, and 428 g. of liquid were collected. Owing to the proximity of their boiling points (100° and 118°, respectively) methyl α-methylacrylate and acetic acid could not be rigorously separated by distillation alone; but 272 g. of crude methyl α-methylacrylate, b. p. 85—106°, were obtained, and a further 10 g. by extraction of the succeeding (acetic acid) fraction with brine. After washing with brine to remove acetic acid, and refractionation, 253 g. of almost pure methyl methylacrylate were obtained, b. p. 96—106° (92% yield, calc. on acetoxy-ester actually destroyed). 21 G. of unchanged acetoxy-ester were recovered, partly by distillation and partly by brine-extraction of the acetic acid fractions.

Methyl α-methylacrylate readily polymerised to a clear hard colourless resin when warmed to 60° with 1% of benzoyl peroxide. The indefinite b. p. recorded above was due to slow partial polymerisation on distillation; but cautious fractionation of a small sample gave a sharper fraction, b. p. 98—102°. The characteristic odour of this ester is unmistakable (1·5840 g. required 32·32 c.c. of N/2-sodium hydroxide. Found : saponification equiv., 98. Calc. for $C_5H_8O_2$: equiv., 100).

The amounts of methyl α-acetoxyisobutyrate " cracked " were approximately 67% at 400°, 95% at 480—500°, and 100% at 560°; at the last temperature there was 16% loss in total weight due to secondary decompositions.

β-Methoxyethyl α-Acetoxyisobutyrate.—Equimolecular amounts of acetone cyanohydrin, water, concentrated sulphuric acid, and " methyl cellosolve " (ethylene glycol monomethyl ether) were refluxed at 80—100°, the ammonium hydrogen sulphate which separated was filtered off, the filtrate distilled in a vacuum, and the β-methoxyethyl α-hydroxyisobutyrate, b. p. 80—100°/20 mm., acetylated with a slight excess of acetic anhydride. Fractionation gave β-*methoxyethyl α-acetoxyisobutyrate* as a colourless mobile liquid, with a pleasant ethereal odour, b. p. 105°/12 mm., $n_D^{24°}$ 1·4210 (Found : C, 52·8; H, 7·8. $C_9H_{16}O_5$ requires C, 52·9; H, 7·8%). Yield, 42%.

Pyrolysis. 200 G. (2 c.c./min.; 450°) gave 192 g. of liquid, which, washed with brine and distilled in a vacuum, yielded 107 g. of pure β-*methoxyethyl α-methylacrylate* (yield, 76%; no unchanged acetoxy-ester was recovered) as a colourless mobile liquid with the characteristic pleasant odour of the α-methylacrylates; b. p. 88—89°/20 mm., $n_D^{24°}$ 1·4283, $d_4^{20°}$ 0·9933 (Found : C, 58·2; H, 8·3. $C_7H_{12}O_3$ requires C, 58·3; H, 8·3%). When heated with 0·5% of benzoyl peroxide, it polymerised to a transparent solid colourless resin.

β-Phenoxyethyl α-Acetoxyisobutyrate.—Equimolecular amounts of acetone cyanohydrin, water, concentrated sulphuric acid, and β-phenoxyethyl alcohol, treated as above, gave a 45% yield of β-*phenoxyethyl α-hydroxyisobutyrate* as a colourless mobile liquid, b. p. 156—157°/5 mm., $n_D^{21°}$ 1·5040, $d_4^{20°}$ 1·1142 (Found : C, 64·5; H, 7·1. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1%). This ester after acetylation gave a 91% yield of β-*phenoxyethyl α-acetoxyisobutyrate* as a colourless, slightly viscous liquid, b. p. 166°/4 mm., $n_D^{21°}$ 1·4910, $d_4^{20°}$ 1·1216 (Found : C, 63·3; H, 6·6. $C_{14}H_{18}O_5$ requires C, 63·2; H, 6·8%).

Pyrolysis. 149 G. of the acetoxy-ester (3 c.c./min.; 500°) gave 134 g. of liquid, which, washed with brine and sodium carbonate and fractionated in a vacuum, yielded 60 g. of pure

β-*phenoxyethyl* α-*methylacrylate* (51% yield; no unchanged acetoxy-ester was recovered) as a colourless mobile pleasant-smelling liquid, b. p. 138°/7 mm., 268°/760 mm., n_D^{20} 1·5160, d_4^{20} 1·0858 (Found : C, 70·0; H, 6·9. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). When maintained for some time just below its b. p., it polymerises to a clear gummy mass.

α-*Acetoxyisobutyronitrile and* N-*Acetyl-α-acetoxyisobutyramide.*—When acetone cyanohydrin is run gradually into acetic anhydride containing acetyl chloride or sulphuric acid as catalyst, the heat of reaction keeps the mixture refluxing gently; by distillation as soon as it has cooled, α-acetoxy*iso*butyronitrile is obtained in 81—86% yield. With perchloric acid as catalyst, the mixture being maintained at 100° for about 5 hours, α-acetoxy*iso*butyronitrile and N-*acetyl-α-acetoxyisobutyramide* are formed each in about 50% yield. The latter is readily isolated, either by distillation in a vacuum, coming over as a rapidly solidifying syrup, b. p. 120—130°/13 mm., or by distillation of the acetoxy-nitrile and crystallisation of the residue from ligroin; it then forms slender colourless prisms and needles (m. p. 81—82°), frequently arranged in rosettes, showing high polarisation colours, no pleochroism, and parallel or symmetrical extinction. It is readily soluble in cold acetone, ether, ethyl alcohol, benzene, chloroform, and carbon tetrachloride and in hot ligroin and water (Found : C, 51·6; H, 7·2; N, 7·4. $C_8H_{13}O_4N$ requires C, 51·3; H, 7·0; N, 7·5%). The molecular weight, determined cryoscopically, was 250, 254, 260 in benzene, 150 in camphor by Rast's method, and 198 in acetic acid (calc., 187).

No appreciable acetylation of acetone cyanohydrin could be effected by glacial acetic acid, with or without catalysts, even on prolonged refluxing with benzene to bring about the azeotropic removal of any water formed (contrast Part I, p. 405).

Pyrolysis of α-*Acetoxyisobutyronitrile.*—287 G. (7 c.c./min.; 425—435°) gave 284 g. of liquid, which on fractionation yielded : (i) 3 g., b. p. < 88°; (ii) 132 g., b. p. 88—98°; (iii) 140 g., b. p. 98—185°; (iv) a small residue. Fraction (i) contained acetone and hydrogen cyanide, identified as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 125—127°, and silver cyanide respectively. Fraction (ii) was slightly crude α-methylacrylonitrile. From fraction (iii), by further fractionation, the higher fractions being washed with brine, 27 g. of α-acetoxy-*iso*butyronitrile were recovered. Fractions (i) and (ii), united and redistilled, gave 132 g. of almost pure α-methylacrylonitrile, b. p. 90—96° (yield, 96%, calc. on the acetoxy-nitrile destroyed); by washing with sodium carbonate solution, drying over phosphoric oxide, and refractionation, a sample was obtained, b. p. 90—90·5°, having an extremely characteristic, unpleasant, fresh, bitter odour (Found : C, 71·5; H, 7·9; N, 20·5. Calc. for C_4H_5N : C, 71·6; H, 7·5; N, 20·9%). This sample polymerised spontaneously to a hard colourless resin after 3 months. A similar sample polymerised and become yellow when heated at 100° for some hours with 1% of benzoyl peroxide.

The secondary formation of acetone and hydrogen cyanide becomes marked at temperatures higher than the above; e.g., 17% of the product of pyrolysis at 550—560° boiled below 78° and contained very little methylacrylonitrile.

Pyrolysis of N-*Acetyl-α-acetoxyisobutyramide.*—51 G. of the amide, dissolved in 130 g. of acetone, were run (5 c.c./min.) into the pyrolysis tube at 515—530°; 161 g. of liquid were collected, from which 123 g. of acetone were recovered by distillation. The remaining 38 g. of liquid, on fractionation, yielded 14 g. of crude methylacrylonitrile and 24 g. of almost pure acetic acid; from the former, on refractionation, 12·5 g. of almost pure material were obtained (65% yield), which readily polymerised (molecular ratio of methylacrylonitrile and acetic acid = 1 : 2).

Methyl α-*Benzoyloxyisobutyrate.*—Benzoyl chloride (286 g.) was added (¾ hour) to methyl α-hydroxy*iso*butyrate (236 g.) and pyridine (160 g.) and after 1 hour the mixture was heated at 100° for 1 hour and poured into cold water. Ether extracted an oil, which, distilled in a vacuum, gave 43 g. of the hydroxy-ester and 324 g. (89% yield) of the desired *benzoyl* derivative. The latter was freed from a small amount of benzoic acid by shaking in ether with dilute sodium carbonate solution, refractionated, and obtained as a colourless, somewhat viscous oil with an aromatic odour; b. p. 124°/4 mm., 156°/19 mm., 205—210°/760 mm., n_D^{20} 1·4992, d_4^{20} 1·120 (Found : C, 64·6; H, 6·1; M, cryoscopic in benzene, 227. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%; M, 222).

Pyrolysis. 108 G. of the ester (4 c.c./min.; 410—420°) gave 100 g. of a pasty yellowish product, which was shaken in ether with sodium carbonate solution; this removed 42 g. of benzoic acid. The ethereal layer was dried and the oil obtained therefrom was distilled, giving (i) 5 g., b. p. < 85°; (ii) 28 g., b. p. 85—101° (mostly 98—100°); (iii) 27 g., b. p. *ca.* 120°/4 mm. Fraction (i) was discarded. From fraction (ii), on refractionation, pure methyl α-methyl-acrylate, b. p. 99—100°, was obtained (Found : saponification equiv., 98. Calc., 100), charac-

terised by its odour and polymerisation. The yields of benzoic acid and methyl methylacrylate were 94% and 77% respectively, calculated on the benzoyloxy-ester destroyed.

Methyl α-Chloroisobutyrate.—This was a by-product in the reaction of carbonyl chloride and methyl α-hydroxyisobutyrate (to be described in Part III). It had b. p. 133—135°/760 mm.

Pyrolysis. 45 G. (2 g./min.; 500—510°) gave hydrogen chloride and 31 g. of a fuming yellowish liquid. This was mostly " uncracked " α-chloro-ester, but distillation gave 5 g. of a liquid, b. p. *ca.* 90—110°, which, washed with aqueous potassium carbonate, had the extremely characteristic odour of methyl methylacrylate and polymerised when warmed for a few hours with 1% of benzoyl peroxide.

Pyrolysis of Acetone Cyanohydrin.—100 G., pyrolysed as above at 510°, yielded 97·5 g. of a mixture of acetone and hydrogen cyanide, b. p. 49—56°.

Pyrolysis of Methyl α-Hydroxyisobutyrate.—250 G. (2·5 c.c./min.; 470—480°) gave 214 g. of liquid, which on fractionation yielded : (i) 27 g., b. p. 50—61°; (ii) 11 g., b. p. 62—94°; (iii) 15 g., b. p. 95—107°; (iv) 11 g., b. p. 107—135°; (v) 144 g., b. p. 136—138°; (vi) a minute residue. Fraction (i) was mainly acetone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 124—126°), and fraction (v) was unchanged hydroxy-ester. Fraction (iii) was crude methyl α-methylacrylate; this together with the crude ester remaining after water-washing of fractions (ii) and (iv), was dried and refractionated, yielding almost pure methyl methylacrylate, b. p. 96—101°.

The total loss of weight on pyrolysis was 14% at 470—480°, 19% at 480—500°, and 26% at 570°.
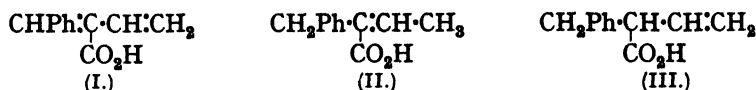
159. *The Modes of Addition to Conjugated Unsaturated Systems. Part VIII. Reduction of α-Vinylcinnamic Acid.*

By CHRISTOPHER K. INGOLD and MAURICE A. T. ROGERS.

THE publication of Part VI completed a general survey of conjugative additions from the point of view of Burton and Ingold's orientation theory of additions; two examples of long standing in which a reported experimental result appeared to present difficulty were considered in Part VII, and we have now examined a recent example.

Kuhn and Deutsch (*Ber.,* 1932, **65,** 817) investigated the reduction of α-vinylcinnamic acid (I) by sodium amalgam; they reported the substantially exclusive formation of the 1 : 4-dihydro-derivative, α-benzylcrotonic acid (II). They suggested that, according to Burton and Ingold's theory, the primary dihydro-product should, on the contrary, be the 1 : 2-isomeride, β-phenyl-α-vinylpropionic acid (III), no trace of which was detected.

$$CHPh\text{:}\overset{|}{C}\cdot CH\text{:}CH_2 \qquad CH_2Ph\cdot\overset{|}{C}\text{:}CH\cdot CH_3 \qquad CH_2Ph\cdot\overset{|}{C}H\cdot CH\text{:}CH_2$$
$$\underset{\text{(I.)}}{CO_2H} \qquad\qquad \underset{\text{(II.)}}{CO_2H} \qquad\qquad \underset{\text{(III.)}}{CO_2H}$$

We accept this application of our views, and return to the matter below, Kuhn and Hoffer (*Ber.,* 1933, **66,** 1263), however, attempted to strengthen their criticism of the theory by the production of a second example : they reduced β-phenylsorbic acid by means of sodium amalgam, and obtained both the 1 : 2- and the 1 : 4-dihydro-compound, in proportions which they determined. They stated that according to Burton and Ingold's theory the 1 : 2-dihydro-isomeride should be produced exclusively. Now *this* is incorrect ; and the conclusion, apparently reached by applying a statement detached from context and implied restrictions, suggests imperfect appreciation of the limitations of the theory. The case, indeed, belongs to a class which, as Burton and Ingold indicated (*loc. cit.,* p. 2025, footnote), is too complicated for theoretical diagnosis. We therefore pass over the criticisms

based on this example, and revert to Kuhn and Deutsch's case, where the issue between theory and reported fact is definite.
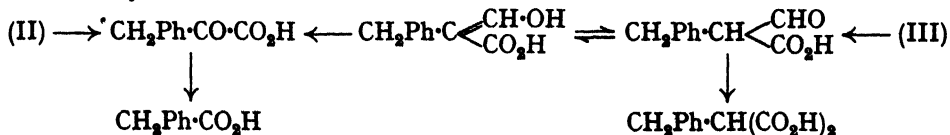
Reduction of α-Vinylcinnamic Acid.—Kuhn and Deutsch reduced the conjugated acid with sodium amalgam in the presence of carbon dioxide. They described the dihydro-acid as a liquid which on distillation (7 mm.) passed into the known crystalline α-benzyl-crotonic acid, m. p. 99°. They suggested that the liquid undistilled acid might contain the unknown geometrical isomeride of the crystalline acid. They considered the presence of β-phenyl-α-vinylpropionic acid to be excluded because (1) on oxidation with chromic acid the liquid acid gave acetic acid in yield equal to that obtained from authentic α-benzyl-crotonic acid, and (2) on ozonolysis the liquid acid gave acetaldehyde but no formaldehyde. We have reinvestigated the matter.

Our reductions of the conjugated acid were carried out with sodium amalgam both in carbonated alkaline, and in acid, solution, and also with aluminium amalgam in neutral solution. All three methods gave similar results. The dihydro-product consisted partly of α-benzylcrotonic acid, m. p. 99°, and partly of a liquid acid. The proportion in which these appeared varied considerably even when the conditions of reduction were as nearly as possible identical. The liquid acid on repeated distillation (14—15 mm.) underwent no change. It was, however, quantitatively converted into α-benzylcrotonic acid, m. p. 99°, when treated with sodium hydroxide. These observations are much more strongly suggestive of prototropic change (a possibility considered by Kuhn and Deutsch) than of geometrical isomerisation (see later). Incidentally, the last experiment proves the absence of the tetrahydro-derivative.

We have excluded the hypothesis that the properties of the liquid dihydro-acid arise from the presence of a labile geometrical isomeride. This isomeride (this vol., p. 723) has m. p. 107°, and none of its mixtures with the acid of m. p. 99° are liquid near the ordinary temperature. Furthermore, the new isomeride is stable, not only thermally, but also on treatment with sodium hydroxide, under conditions more drastic than those of the experiments with the liquid dihydro-acid.

The oxidative degradation of the liquid acid was accomplished partly by Burton and Ingold's method (J., 1929, 2022) and partly by Fischer, Düll, and Ertel's (*Ber.*, 1932, **65**, 1467); the former yielded an acid corresponding to the aromatic fragment of the unsaturated molecule, and the latter an aldehyde representing the aliphatic fragment. We show by both methods that the essential constituent of the liquid acid is indeed β-*phenyl-α-vinylpropionic acid* (III).

Burton and Ingold's method consists in ozonolysis combined with oxidation by hydrogen peroxide. Probably all specimens of the liquid acid contained some dissolved α-benzyl-crotonic acid, not wholly removed by freezing or by fractional solution in water, and the oxidation product from this acid was phenylacetic acid. The β-phenyl-α-vinylpropionic acid also yielded some phenylacetic acid, especially when alkali was present during the oxidation of the aldehydes; but under suitably adjusted conditions, it gave its characteristic product, benzylmalonic acid :

$$(II) \longrightarrow \cdot CH_2Ph \cdot CO \cdot CO_2H \longleftarrow CH_2Ph \cdot C\begin{array}{l}CH \cdot OH \\ CO_2H\end{array} \rightleftharpoons CH_2Ph \cdot CH\begin{array}{l}CHO \\ CO_2H\end{array} \longleftarrow (III)$$

$$\downarrow \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow$$

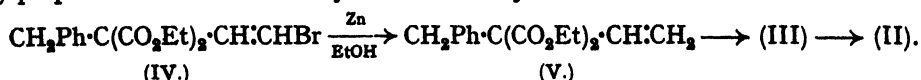$$CH_2Ph \cdot CO_2H \qquad\qquad\qquad\qquad\qquad CH_2Ph \cdot CH(CO_2H)_2$$

The intervention of the hydroxymethylene tautomeride of the aldehydic acid is assumed in order to account for effect of alkalis on the course of the oxidation of β-phenyl-α-vinylpropionic acid.

It appears, as might have been expected from the constitution of β-phenyl-α-vinyl-propionic acid, that its ozonide is thermally unstable : the liquid dihydro-acid, on ozonoly-sis under ordinary conditions, yields only a little acetaldehyde, derived from the dissolved α-benzylcrotonic acid, but no formaldehyde. Fischer, Düll, and Ertel's method of ozonoly-sis is particularly valuable in cases of this kind (cf. Bradfield, Francis, and Simonsen, J., 1934, 188), and on applying it to the liquid acid we obtained formaldehyde in good yield.

These results prove that the liquid dihydro-compound consists essentially of β-phenyl-α-vinylpropionic acid (III). Its conversion into the Δ^α-tautomeride (II) has already been described and below we give synthetic confirmation of the facility with which this change takes place. We also show that in the reduction of a simple analogue of α-vinylcinnamic acid, for which, however, the change corresponding to (III) —→ (II) is much less facile, the sole dihydro-product is the 1 : 2-derivative, as theory requires.

Formation and Decarboxylation of Ethyl Benzylvinylmalonate.—The preparation was based on Cope and McElvain's discovery (*J. Amer. Chem. Soc.*, 1932, **54**, 4311) that dibromo-ethylene has an appreciable reactivity towards sodiomalonic esters. Condensation with ethyl potassiobenzylmalonate yielded the *bromovinyl* ester (IV), which on reduction with zinc and alcohol gave the *vinyl* ester (V). On hydrolysis of this, with either alkalis or acids, decarboxylation took place accompanied by complete isomerisation of the β-phenyl-α-vinylpropionic acid to the ordinary form of α-benzylcrotonic acid :

$$CH_2Ph \cdot C(CO_2Et)_2 \cdot CH\text{:}CHBr \xrightarrow[\text{EtOH}]{\text{Zn}} CH_2Ph \cdot C(CO_2Et)_2 \cdot CH\text{:}CH_2 \longrightarrow (III) \longrightarrow (II).$$
$$\text{(IV.)} \qquad\qquad\qquad\qquad \text{(V.)}$$

Reduction of α-Styrylcinnamic Acid.—The theory that the primary product of amalgam reductions of α-vinylcinnamic acid should be the 1 : 2-dihydro-compound applies equally to any substitution product of this acid, provided that it does not contain an additional substituent comparable in function with the carboxyl group; and amongst such substitution products some should be discoverable for which the transformation of the 1 : 2- into the 1 : 4-dihydro-derivative is much less facile than for α-vinylcinnamic acid itself. An example exists in α-styrylcinnamic acid (VI). Thiele reduced this substance by means of sodium amalgam in acid solution, and obtained only the 1 : 2-dihydro-compound (VII) (*Annalen*, 1899, **306**, 225). We have confirmed this observation, and also have carried out the reduction in alkaline solution with an identical result.

$$\text{(VI)} \quad CHPh\text{:}C(CO_2H) \cdot CH\text{:}CHPh \longrightarrow CH_2Ph \cdot CH(CO_2H) \cdot CH\text{:}CHPh \quad \text{(VII)}$$
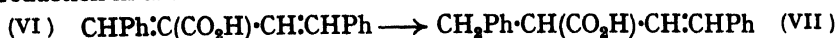
Concluding Remarks.—It will be appreciated that the theory of amalgam reductions is part of a more general theory of addition, in conformity with the principles of which it is assumed that the hydrogen adds, not in an atomic, but in an ionic, manner, the components ($\overset{+}{H} + 2e$) of the unstable ion ($\overset{-}{H}$) being fixed before the complementary, stable ion ($\overset{+}{H}$) is taken up. Kuhn and Hoffer (*loc. cit.*) reject this conception in favour of that of the addition of hydrogen atoms or sodium atoms, and in their argument they allude to the statistical improbability of triple collisions, to the occurrence of pinacol-like reduction, and to known effects of the purity of amalgams. In reply we would direct attention to the statistical equivalence of three-body and successive two-body collisions (Hinshelwood, " Kinetics of Homogeneous Gas Reactions," 1933, p. 157). We should also emphasise that in our view the hydrogenation is essentially a wall-reaction, and that, in conformity with well-established conceptions, the metal surface is assumed to be present throughout the rate-affecting stage, normally the fixation of $\overset{-}{H}$. Even the pinacol-like reduction products are formed only when two neighbouring adsorbed molecules, each having acquired but one electron from the metal, can be desorbed in combination ; and when secondary changes succeed addition, as in the example of α-vinylcinnamic acid, they may also occur before or during desorption. The effect of purity in amalgams is automatically covered. Electrically conducting impurities provide weak places in the work-function of the metal–electrolyte interface, and, if these suffice for the electrons to escape into the electrolyte without using the reducible organic substance as a path, the amalgam will have poor efficiency. On the other hand, if, owing to the absence of electrically conducting impurities, the potential wall is nearly electron-proof, the discharge will be dependent on the adsorption of a molecular electrical conductor, *i.e.*, an unsaturated compound, and the reducing efficiency will be high. The theory is, indeed, in excellent agreement with the available facts, and one of its advantages over atomic theories of amalgam reductions is that it can be closely linked with contemporary views on overpotential.

α-Vinylcinnamic Acid.—This was prepared as recommended by Kuhn and Ishikawa (*Ber.*, 1931, **64**, 2347) except that an atmosphere of nitrogen was maintained above the reaction mixture in order to avoid the formation of coloured oxidation products. Amorphous by-products were removed by crystallising the crude acid from a large volume (*e.g.*, 24 l. for 15 g. of acid) of water below 75°, this limit of temperature being necessary to avoid polymerisation. The acid then separated from light petroleum in stout needles, and from acetic acid in plates, m. p. 92°. The yield was variable, and seldom above 20%.

Reduction of α-Vinylcinnamic Acid.—The sodium amalgam (2·5%) was in a readily friable form, prepared under paraffin in porcelain vessels. Various samples of aluminium were used for the preparation ("Houben," II, 256) of aluminium amalgam, one of the most satisfactory being a foil supplied by Messrs. Harrington Bros. The α-vinylcinnamic acid was reduced by sodium amalgam in alkaline and in acid solution and by aluminium amalgam in neutral solution. A typical reduction of each kind is described below, but the proportion of liquid product varied in the different experiments of each series.

(a) A solution of the acid (4·3 g.) in 2*N*-sodium carbonate (1 equiv.) was diluted with water (200 c.c.), treated with a stream of carbon dioxide, and stirred for 3·5 hours, during the first 2 hours of which the amalgam (450 g.) was gradually introduced. Hydrochloric acid was added to the filtered solution at 0°. The precipitate, which was washed with much water and crystallised from this solvent, consisted of α-benzylcrotonic acid, and a further small quantity, isolated along with the liquid acid, was separable below 0° (m. p. and mixed m. p. 99°; yield, 2·1 g.). The liquid acid, obtained by extraction of the aqueous liquors with ether, was purified by two distillations (b. p. 119—122°/2 mm., 174°/19 mm.; yield, 1·5 g.) (Found: C, 74·7; H, 6·9. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%).

(b) For the reductions in acid solution the solvent was a mixture of 95% ethyl alcohol (80 c.c.) and glacial acetic acid (60 c.c.). At the end of the reduction the mixture was filtered, and the residues washed with hot alcohol and acetic acid. Water was added to the solution, the alcohol boiled off, and hydrochloric acid added at 0°. The products, isolated as under (a), were α-benzylcrotonic acid (0·75 g., m. p. 99°) and the liquid acid (2·25 g., b. p. 166°/15 mm.), from which no further α-benzylcrotonic acid could be separated.

(c) A neutral solution of the acid (5·7 g.) in 2*N*-aqueous sodium hydroxide was diluted with water (500 c.c.) and reduced for 18 hours with aluminium amalgam (13 g.). The products were α-benzylcrotonic acid (3·5 g.) and the liquid acid (1·3 g.).

Properties of the Liquid Dihydro-Acid.—Specimens from which further α-benzylcrotonic acid could not be separated by freezing or otherwise could not be caused to yield that acid by distillation (15 mm.), followed by cooling and seeding. They were, however, quantitatively converted into the pure crystalline acid by treatment with 2*N*-aqueous sodium hydroxide for 15 minutes on the water-bath. The same reagent effected conversion, although more slowly, at room temperature. The liquid acid and α-benzylcrotonic acid were comparably hydrogenated in 95% ethyl alcohol in the presence of Adams's platinum catalyst; both absorbed nearly 4 mols. of hydrogen and the times occupied in the absorption were similar.

Oxidation of the Liquid Dihydro-acid.—(a) The acid was treated with 3% ozonised oxygen in chloroform solution at 0°, and after removal of the solvent the ozonides were decomposed with water. Volatile aldehydes were carried by means of a stream of air into a solution of 2 : 4-dinitrophenylhydrazine in 2*N*-hydrochloric acid. The precipitated arylhydrazones appeared to be impure, but by crystallisation from alcohol and benzene gave acetaldehyde-2 : 4-dinitrophenylhydrazone. The remaining products of the ozonolysis were oxidised with hydrogen peroxide (Burton and Ingold, *loc. cit.*). The acids, obtained by extraction with ether, were lixiviated with water, which removed the more soluble benzylmalonic acid, and this was then extracted from the aqueous washings with ether and crystallised from benzene (m. p. and mixed m. p. 115°) (Found: C, 62·0; H, 5·2. Calc.: C, 61·9; H, 5·2%). The acid which was less soluble in water was crystallised from ligroin and shown to be phenylacetic acid (m. p. and mixed m. p. 76°). If sodium carbonate or hydroxide was added before the decomposition of the ozonides with water, the sole acid product was phenylacetic acid.

(b) The acid was treated with 3% ozonised oxygen in ethyl acetate at − 80°, and the ozonides were reduced with hydrogen after the addition of palladised barium sulphate (Fischer, Düll, and Ertel, *loc. cit.*). The filtered solution was extracted with water, and formaldehyde was isolated from the aqueous extract in the form of methylenedimethone (Vorländer, *Z. anal. Chem.*, 1929, **77**, 241) (m. p. and mixed m. p. 188—189°).

Ethyl α-Vinylcinnamate.—Silver α-vinylcinnamate (20 g., prepared from a neutral solution of the ammonium salt), ethyl iodide (26 g.), and benzene (100 g.) were heated together on the water-bath for 1·5 hours, and the filtered solution was dried and evaporated. The drying was necessary because it was not found possible to remove water completely from the silver salt by exposure over phosphoric oxide in a vacuum, and it is undesirable to heat the salt. The *ester* was a sweet-smelling liquid, b. p. 106—108°/1 mm. (Found : C, 76·9; H, 6·9. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9%). On reduction with an equal weight of aluminium amalgam in moist ether, a *dihydro*-derivative, b. p. 134—144°/13—14 mm., was obtained (Found : C, 76·1; H, 8·1. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·9%).

Reduction of α-Styrylcinnamic Acid.—(a) The reduction by sodium amalgam in alcoholic acetic acid, described originally by Thiele (*loc. cit.*), was repeated with the same results; the β-phenyl-α-styrylpropionic acid, m. p. 124°, obtained in good yield, was converted by means of bromine into 2-bromo-1-phenyl-*ac*-tetrahydronaphthalene-3-carboxylic acid.

(b) Thiele stated that reduction in alkaline solution is precluded by the sparing solubility of sodium styrylcinnamate in water. Trial showed that the sodium salt is soluble enough, but that the acid is so weak that it is precipitated from an alkaline solution by carbon dioxide; it is, indeed, soluble in sodium carbonate, but not in sodium hydrogen carbonate, so an excess of carbon dioxide cannot be passed during the reduction. We therefore reduced the acid without carbonating. It was dissolved (3 g.) in 2N-sodium carbonate (12 c.c.), and the solution, diluted to 1 l., was treated during 3 hours with 3% sodium amalgam (50 g.). Rapid stirring was maintained, and after a further 2 hours the filtered solution was acidified. The precipitated product was treated as under (a) with the same results.

β-Phenyl-α-styrylpropionic acid remained substantially unchanged when heated under reflux for 2 hours with excess of 5N-aqueous sodium hydroxide.

Ethyl Benzyl-β-bromovinylmalonate.—No product of even approximately the correct bromine content could be obtained from *s.*-dibromoethylene and ethyl sodiobenzylmalonate (cf. Cope and McElvain, *loc. cit.*). The bromovinyl compound was, however, obtained in a sufficiently pure form for further work by the following method. An ethereal solution of ethyl benzyl-malonate (75 g.) was warmed with potassium (11·7 g.) under reflux until the metal had completely dissolved, and dibromoethylene (112 g.) was then added. The reaction appeared to begin readily, notwithstanding that a large amount of unchanged material was always recovered. The mixture was heated under reflux with continuous stirring for 18 hours, and the ethereal solution was then washed with dilute hydrochloric acid and with sodium chloride solution and dried with sodium sulphate. The ether and unchanged dibromoethylene were distilled off at ordinary pressure, and the unchanged ethyl benzylmalonate in the vacuum of a water pump. The condensation product, isolated by distillation up to about 165° at pressures below 0·1 mm., was obtained by redistillation as a pale yellow, viscous oil, b. p. 130—140°/0·05—0·07 mm. (Found : Br, 20·4. $C_{16}H_{19}O_4Br$ requires Br, 22·6%). The yields were about 7% of the theoretical.

Ethyl Benzylvinylmalonate.—A mixture of the bromo-ester (7 g.), 95% ethyl alcohol (15 c.c.), and zinc dust (4 g.) was enclosed in a stout sealed tube, which was clamped perpendicularly to a shaft by means of which it was slowly rotated for 10 hours in an air-bath at 170°. The cooled tube was opened (a considerable pressure was released), and the filtered solution was evaporated. The product from two experiments was washed in ethereal solution with hydrochloric acid, dried, and distilled. The required *ester* (4·5 g.) was collected at 100—110°/0·14 mm. (Found : C, 69·5; H, 7·2. $C_{16}H_{20}O_4$ requires C, 69·6; H, 7·2%).

The ester was hydrolysed with ethyl-alcoholic potassium hydroxide, aqueous-alcoholic sodium hydroxide, aqueous barium hydroxide, and hydrochloric acid in aqueous acetic acid. The sole product in all cases was α-benzylcrotonic acid (m. p. and mixed m. p. 99°).

160. *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XXII. Wagner Rearrangement in the Hofmann Degradation.*
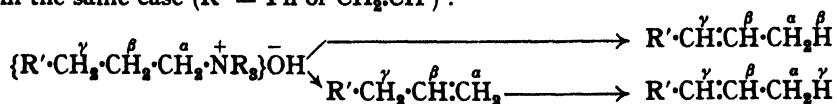
By Christopher K. Ingold and Maurice A. T. Rogers.

Although this series has been largely concerned with the study of β-hydrogen elimination from 'onium salts, illustrations have been given of the alternative of α-elimination with accompanying dimerisation. The remaining alternative, *viz.*, γ-elimination with an accompanying Wagner rearrangement, is now demonstrated :

$$\{R'R''CH\cdot\overset{+}{N}R_3\}\overset{-}{X} \longrightarrow (R'R''C\!:)_2 \qquad + HX + NR_3 \text{ (α-elimination)}$$

$$\{R'R''CH\cdot CH_2\cdot\overset{+}{N}R_3\}\overset{-}{X} \longrightarrow R'R''C\!:\!CH_2 \qquad + HX + NR_3 \text{ (β-   ,,   )}$$

$$\{R'R''CH\cdot CH_2\cdot CH_2\cdot\overset{+}{N}R_3\}\overset{-}{X} \longrightarrow R'R''C\!:\!CH\cdot CH_3 + HX + NR_3 \text{ (γ-   ,,   )}$$
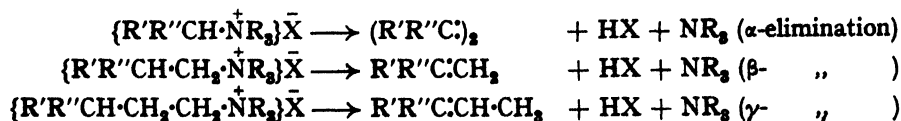
β-Elimination is the normal reaction, involving neither octet disruption nor regrouping of atomic nuclei. It has been shown that α-elimination, which involves octet disruption, necessitates facilitating constitutional conditions. A similar requirement may be expected for γ-elimination, which entails atomic rearrangement.
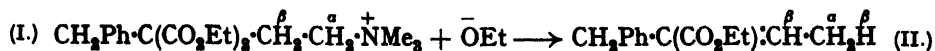
Phenyl groups are known to activate an adjacent hydrogen atom, and γ-elimination might therefore be suspected in the decomposition of γ-phenyl-*n*-propyltrimethylammonium hydroxide, the olefin produced having the correct constitution (Senfter and Tafel, *Ber.*, 1894, **27**, 2309). On the other hand, the same olefin might also arise as the result of a β-elimination, followed by prototropic change of a type which the phenyl group is also known to promote. The formation of piperylene by the exhaustive methylation of piperidine is in the same case (R' = Ph or $CH_2\!:\!CH\cdot$) :

$$\{R'\cdot\overset{\gamma}{CH_2}\cdot\overset{\beta}{CH_2}\cdot\overset{\alpha}{CH_2}\cdot\overset{+}{N}R_3\}\overset{-}{OH} \underset{R'\cdot\overset{\gamma}{CH_2}\cdot\overset{\beta}{CH}\!:\!\overset{\alpha}{CH_2}\longrightarrow R'\cdot\overset{\gamma}{CH}\!:\!\overset{\beta}{CH}\cdot\overset{\alpha}{CH_2}\overset{\gamma}{H}}{\overset{R'\cdot\overset{\gamma}{CH}\!:\!\overset{\beta}{CH}\cdot\overset{\alpha}{CH_2}\overset{\beta}{H}}{\Bigg\diagdown}}$$

The difficulty of distinguishing between these mechanisms arises from the circumstance that the eliminated atom and the atom which migrates are both hydrogen. In the above formulæ the hydrogen atoms are labelled according to their position in the original compound, and it is seen that, whereas in one mechanism a γ-hydrogen atom is eliminated whilst a β-atom migrates, in the other the reverse is true. (Actually the position is further complicated by the presence of displaceable hydrogen in the anion, but this is not essential : the anion might have been ·OĒt, ·OPh, etc.) The site of the elimination and of the migration could, of course, be determined by an isotopic labelling of hydrogen, but the method employed in this paper is to replace one pair of hydrogen atoms by altogether different groups, which, however, like hydrogen, can undergo elimination in a positive form under the attack of a nucleophilic anion.
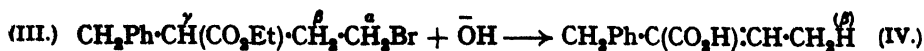
It is known that many substituted malonic and cyanoacetic esters, on treatment with ethoxide ions in alcohol, eliminate a carbethoxyl group as ethyl carbonate, just as substituted acetoacetic esters lose an acetyl group as ethyl acetate in the familiar retrogression of the Claisen reaction. Evidently, the reagent EtŌ, removes these groups in a positive form to give EtO·CO₂Et and EtO·Ac, just as it removes the proton to give EtO·H.

The simplest demonstration of γ-elimination becomes possible if the group which is to undergo elimination instead of hydrogen is placed in the γ-position to the ammonium residue : the stoicheiometry of the reaction reveals its character. We have used the carbethoxyl group for the elimination, with ethoxide as the attacking anion, and the result demonstrates γ-elimination with Wagner rearrangement involving migration of hydrogen :

(I.) $CH_2Ph\cdot C(CO_2Et)_2\cdot\overset{\beta}{CH_2}\cdot\overset{\alpha}{CH_2}\cdot\overset{+}{N}Me_3 + \overset{-}{O}Et \longrightarrow CH_2Ph\cdot C(CO_2Et)\!:\!\overset{\beta}{CH}\cdot\overset{\alpha}{CH_2}\overset{\beta}{H}$ (II.)

The study of this reaction assists the interpretation of another elimination that we have

examined, which at first sight appears equivocal, as the removal either of γ-hydrogen with Wagner rearrangement or of β-hydrogen with prototropy could account for the structure of the product :

(III.) $CH_2Ph\cdot\overset{\gamma}{C}H(CO_2Et)\cdot\overset{\beta}{C}H_2\cdot\overset{\alpha}{C}H_2Br + \bar{O}H \longrightarrow CH_2Ph\cdot C(CO_2H){:}CH\cdot CH_2\overset{(\beta)}{H}$ (IV.)

The following argument, however, makes it very probable that this reaction also involves γ-elimination. An acid of structure (IV) can evidently exist in two stereoisomeric forms : one of these has long been known, and the other, distinguished by the prefix *iso-*, is now described for the first time. Both the ester (II) and the acid (IV) have the *iso*-configuration. The indication of this comparison, *viz.*, that both ester and acid are produced by an analogous mechanism, is strengthened by the observation (this vol., p. 718) that when an acid of structure (IV) is actually produced by a simple prototropic change (or by a composite reaction which obviously involves one) it has its ordinary and not the *iso*-configuration. Evidently prototropy can scarcely be assumed in the reaction (III) $\longrightarrow$ (IV), and the whole group of observations is interpreted consistently if it is supposed that the Wagner change in systems of the type of (I) and (III) uniformly leads to products of the *iso*-configuration.

The preparative work involved in these studies is summarised in the following scheme :

$$CH_2Ph\cdot CNa(CO_2Et)_2 + CH_2Cl\cdot CH_2\cdot NMe_2 \longrightarrow CH_2Ph\cdot C(CO_2Et)_2\cdot CH_2\cdot CH_2\cdot NMe_2$$
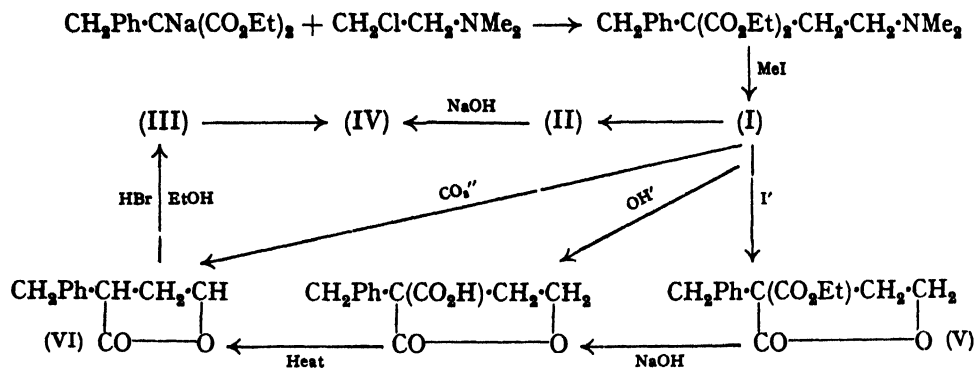
The complementary product accompanying (V), trimethylethylammonium iodide, was isolated. The constitution of (VI) was confirmed by oxidation with permanganate to benzylsuccinic acid. The constitution of the *iso*-acid (II) follows from the fact that, like the ordinary form of the acid, it gave acetaldehyde on ozonolysis.

EXPERIMENTAL.

Formation of Ethyl Trimethyl-δ-phenyl-n-butylammonium-γγ-dicarboxylate Salts.—β-Hydroxy-ethyldimethylamine was prepared by the following modification of the method described by Hanhart and Ingold (J., 1927, 1012). Ethylene oxide (25 g.) was slowly added with shaking and external cooling to a solution (80 g.) of dimethylamine (330 g. per l.) previously diluted with ice-water. Solid potassium hydroxide was added until a layer of amine separated, and this was then extracted with ether. The extract was dried with potassium hydroxide, the amine being distilled over barium oxide and collected within the range 125—136°. If the drying of the base with potassium hydroxide were prolonged or if sodium hydroxide were used, voluminous precipitates appeared. The compositions of these were not sufficiently constant to justify any suggestion concerning their constituents.

β-Chloroethyldimethylamine hydrochloride, m. p. 200°, was prepared by treatment of the hydroxy-amine with thionyl chloride in chloroform (*idem, ibid.*). Attempts to condense the chloroamine with malonic esters in the presence of alcoholic sodium ethoxide led to the formation of β-ethoxyethyldimethylamine. After removal of the sodium chloride by filtration, evaporation of most of the alcohol and addition of ether, the hydrochloride of this base was precipitated by means of dry hydrogen chloride as a white gum. From this the base was liberated and treated with methyl iodide in ether. The β-*ethoxyethyltrimethylammonium iodide*, crystallised from amyl alcohol, had m. p. 156—158° (Found : C, 32·6; H, 6·9; N, 4·7. $C_7H_{18}ONI$ requires C, 32·4; H, 6·9; N, 5·4%).

Ethyl benzylmalonate (25 g.), b. p. 168—170°/15 mm., was digested with finely divided sodium (2·2 g.) under xylene until the metal had dissolved. β-Chloroethyldimethylamine hydrochloride (11·8 g.) was purified in water, and the amine extracted with ether and dried in this solvent by shaking with potassium carbonate for ¼ hour. The ether was distilled off, the last 25 c.c. being removed at the ordinary temperature in a vacuum, and xylene was added. Under these conditions polymerisation does not occur and, on mixing the solution with the xylene solution of the ester, condensation commences. The mixture was gently warmed, and then heated under reflux for 2 hours in order to polymerise any excess of chloro-amine. Water and ether were added, and the ether–xylene solution was extracted with dilute hydrochloric acid. The ethyl benzyl-β-dimethylaminoethylmalonate precipitated as an oil by basification was collected in ether. It could not be crystallised or distilled. Its *hydrochloride* crystallised from chloroform in plates, m. p. 131—132°, having a strong tendency to retain the solvent (Found : C, 59·5; H, 7·9; Cl, 12·0. $C_{18}H_{27}O_4N,HCl$ requires C, 60·3; H, 7·8; Cl, 10·0%).

The *methiodide* was prepared in nitromethane solution, and was precipitated by addition of ether as a slowly solidifying gum. This was dissolved in the minimal amount of hot chloroform, and the filtered solution was mixed, after cooling, with 5—6 volumes of benzene. The iodide then slowly crystallised in small plates, which, even after drying in a vacuum at 60°, contained benzene and had an unsharp m. p. in the range 103—130° [Found : C, 51·9, 51·7; H, 6·6, 6·6; N, 2·5; I, 25·1. $3(C_{19}H_{30}O_4NI),C_6H_6$ requires C, 51·5; H, 6·6; N, 2·8; I, 25·3%]. The iodide was more soluble in alcohol, acetone and chloroform than in water, and was appreciably soluble in benzene. The chloride was prepared from the iodide by digestion with silver chloride in aqueous alcohol. The filtered solution was evaporated to dryness, and the residue was caused to solidify by washing with ether, and then taken up in chloroform. The chloride was then caused to crystallise by the addition of benzene, and was shown to be free from iodide. Aqueous solutions of the hydroxide and carbonate were prepared from the iodide and the appropriate silver compounds. An alcoholic solution of the ethoxide was obtained from the chloride and alcoholic sodium ethoxide, the sodium chloride being removed with the aid of a centrifuge.

Thermal Decomposition of Salts of Ethyl Trimethyl-δ-phenyl-n-butylammonium-γγ-dicarboxylate.—(a) A solution of the hydroxide was evaporated to dryness and the residue was heated at 140—170° for 2 hours in a slow stream of nitrogen. The evolved trimethylamine was identified and the residue was extracted with ether, and divided into acid, basic and neutral fractions by means of aqueous hydrochloric acid and sodium carbonate. A more satisfactory preparation of the acid product is described under (b). The basic product was ethyl benzyl-β-dimethylaminoethylmalonate, identified as its methiodide. The neutral product was an oil, b. p. 180—182°/15 mm., and was identified by its properties and oxidation as *α-benzyl-γ-butyrolactone* (Found : C, 74·7; H, 6·8; *M*, Rast, 179, 182. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%; *M*, 176). The lactone is insoluble in cold dilute sodium hydroxide, and only slowly soluble in the warm reagent.

(b) A solution of the hydroxide together with sodium hydroxide in excess of the amount necessary for the hydrolysis of the carbethoxyl groups was evaporated to dryness, and the residue heated at 140° for 2 hours. The residue was taken up with water and the filtered solution was strongly acidified with hydrochloric acid. The *α-benzyl-γ-butyrolactone-α-carboxylic acid*, precipitated as an oil, was collected in ether, and, after removal of the solvent, was kept over phosphoric oxide until solid. It crystallised from carbon tetrachloride, or from a large volume of carbon disulphide, in needles, m. p. 87—88° (Found : C, 65·3; H, 5·4; *M*, Rast, 190. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·4%; *M*, 220). The acid is soluble in water, acetone and benzene, but insoluble in ligroin. At 125—140° it evolves carbon dioxide, the residue being α-benzyl-γ-butyrolactone.

(c) A solution of the carbonate was evaporated, and the residue was decomposed at 125—150° in a slow stream of carbon dioxide. The product, taken up in ether and distilled, b. p. 186—188°/17 mm., was α-benzyl-γ-butyrolactone.

(d) The iodide was heated for 2 hours at 160—200°. The issuing gases were passed through dilute hydrochloric acid, but the amount of base thus collected was small. The residue was washed with ether, and the extract washed with dilute hydrochloric acid, which removed a small amount of ethyl benzyl-β-dimethylaminoethylmalonate. The residue obtained on removal of the ether was separated by distillation into two fractions, the more volatile of which was usually the larger in amount, although the proportions varied in the different experiments. The more volatile fraction was ethyl *iso*-α-benzylcrotonate, described under (e); the less volatile was ethyl α-benzyl-γ-butyrolactone-α-carboxylate. The esters were identified by hydrolysis with alcoholic potassium hydroxide to the corresponding acids. The residue which

was insoluble in ether was a mixture of tetramethylammonium iodide (Found : C, 24·1; H, 5·9; I, 63·1. Calc. : C, 23·9; H, 6·0; I, 63·2%) and trimethylethylammonium iodide (Found : C, 27·1; H, 6·6; I, 58·3. Calc. : C, 27·9; H, 6·5; I, 59·2%), which were separated by means of chloroform, in which the former salt is insoluble; the first was crystallised from aqueous alcohol, and the second from absolute alcohol.

(e) An alcoholic solution of the ethoxide was evaporated to dryness, and the residue was heated for 2 hours at 150—210°. The product, taken up in ether and washed with dilute hydrochloric acid, yielded *ethyl iso-α-benzylcrotonate*, b. p. 144—148°/19 mm. (Found : C, 76·2; H, 7·7. $C_{13}H_{16}O_2$ requires C, 76·6; H, 7·8%). This was hydrolysed by means of both aqueous and aqueous-alcoholic potassium hydroxide, and on acidification *iso-α-benzylcrotonic acid* was precipitated as a rapidly solidifying oil. The acid crystallised from light petroleum in oblique prisms, m. p. 107° (Found : C, 75·0; H, 6·8. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%. For the *silver* salt : Found : Ag, 37·9. $C_{11}H_{11}O_2Ag$ requires Ag, 38·2%), and its amide, prepared by way of the chloride, separated from benzene–ligroin in plates, m. p. 82—83°. α-Ethylcinnamic acid, m. p. 104°, was prepared for comparison : a mixture with the acid of m. p. 107° melted at about 70°.

Conversion of α-Benzyl-γ-butyrolactone into iso-α-Benzylcrotonic Acid.—A solution of the lactone in ethyl alcohol was saturated with hydrogen bromide. The solvent was removed by warming in a vacuum, and the residual bromo-ester was hydrolysed by boiling for several hours with 20% aqueous-alcoholic sodium hydroxide. The acid, m. p. and mixed m. p. 107°, was obtained as a precipitate on acidification.

Oxidation of α-Benzyl-γ-butyrolactone.—A solution of the lactone in sodium hydroxide was mixed with a slight excess of 3% permanganate solution. The next day the residual permanganate was destroyed with sulphur dioxide, and the solution was worked up for acids. The benzylsuccinic acid, isolated by extraction with ether, and purified by washing with benzene and crystallisation from water, had m. p. (and mixed m. p.) 159—160°.

Properties of iso-α-Benzylcrotonic Acid.—The acid showed no sign of any change either on heating at temperatures up to 250°, or on boiling for 8 hours with 20% aqueous potassium hydroxide. On treatment with ozonised oxygen in chloroform at 0° an ozonide was formed, which evolved acetaldehyde on warming with water. The aldehyde was identified (m. p. and mixed m. p.) as its 2 : 4-dinitrophenylhydrazone (Found : C, 43·0; H, 4·0. Calc. : C, 42·9; H, 3·6%).

UNIVERSITY COLLEGE, LONDON.   [*Received, February 27th*, 1935.]

NOTES.

Derivatives of o-Piperonal. By THOMAS S. STEVENS.

PERKIN and TRIKOJUS (J., 1926, 2925) prepared some simple derivatives in this series from *o*-piperonylic acid (IV), derived ultimately from *o*-vanillin. Compounds of the same class can be obtained in moderate yield from dibromocatechol methylene ether (I) (Jones and Robinson, J., 1917, **111**, 913) as follows :
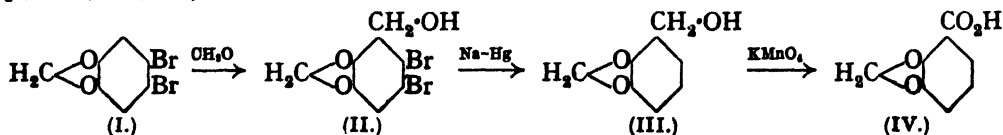
2 : 3-*Dibromo*-5 : 6-*methylenedioxybenzyl Alcohol* (II).—A mixture of acetic acid (250 c.c.), concentrated sulphuric acid (70 c.c.), and formalin (25 c.c. of 38%) was added to dibromo-catechol methylene ether (30 g.) in hot chloroform (30 c.c.), and the whole kept at 40° for 2 weeks. It was diluted with water and extracted with chloroform, the extract washed with water and sodium carbonate solution, and the chloroform evaporated. The residue was heated for several hours with alcoholic potash to hydrolyse the acetyl derivative of (II), and unchanged (I) distilled in steam. The non-volatile resinous solid was extracted with hot 70—80% methyl alcohol; the extracts, boiled with charcoal and concentrated, yielded the *dibromo-alcohol*, which formed prisms from benzene, m. p. 115° (Found : Br, 51·5. $C_8H_6O_3Br_2$ requires Br, 51·6%).

3 B

o-Piperonyl Alcohol (2 : 3-*Methylenedioxybenzyl Alcohol*) (III).—The foregoing alcohol, in boiling 70% methyl alcohol (20 parts), was reduced with sodium amalgam (50—60 parts of 3%), most of the alkali formed being neutralised with acetic acid. The mixture was concentrated somewhat and extracted with ether, and the dried extract distilled. *o-Piperonyl alcohol*, b. p. 165°/30 mm., crystallised from benzene–ligroin in needles, m. p. 34—35° (Found : C, 63·2; H, 5·5. $C_8H_8O_3$ requires C, 63·2; H, 5·3%). It dissolved readily in benzene and sparingly in hot water; oxidised by aqueous permanganate, it yielded o-piperonylic acid, identical (mixed m. p.) with a specimen prepared according to Perkin and Trikojus. With hot, very dilute chromic acid mixture, it gave o-piperonal, identified as the p-nitrophenyl-hydrazone, which had the properties ascribed to it by the same authors.—THE UNIVERSITY, GLASGOW. [*Received, March 21st,* 1935.]

The Odd-membered n-*Primary Alcohols* (*The* α ——➤ β *Transition*). By THOMAS MALKIN. IN a recent paper dealing with the dimorphism of certain aliphatic compounds (J., 1934, 1661, par. 3) Phillips and Mumford state that their results " show definitely " that the odd alcohols above C_{14} exist in a β-tilted form, and that Malkin's conclusions (*J. Amer. Chem. Soc.*, 1930, 52, 3739), which indicate a vertical chain and are based on X-ray measurements, " would appear to be based on a misinterpretation."

It is not at all clear how Phillips and Mumford come to these conclusions, but it can be stated quite definitely that there is no evidence in support of their claim.

As is well known, the question of the tilt of the chain in solid long-chain compounds can only be decided by X-ray investigation; yet, notwithstanding the positive terms of their criticism, Phillips and Mumford do not adduce a single X-ray measurement. On the other hand, the X-ray results published in the above paper have been repeated, confirmed, and extended by Wilson and Ott (*J. Chem. Physics*, 1934, 2, 231) and further extended and confirmed by Piper, Chibnall, and Williams (*Biochem. J.*, 1934, 28, 2175). Thus, three independent investigations have established that the chains in odd alcohols are always vertical.

The evidence which Phillips and Mumford consider sufficient to refute this body of X-ray data is the observation that odd alcohols undergo an α ——➤ β transition, a few degrees below the melting point, and it is clear from the text that they are under the impression that the mere existence of a β-form is *proof* of a tilted chain. This view is, however, based on an erroneous assumption that all β-forms possess tilted chains. Muller has shown that the β-forms of odd paraffins possess vertical chains (*Proc. Roy. Soc.*, 1928, *A*, 120, 437; 1930, *A*, 127, 417; 1932, *A*, 138, 514).

The correct explanation of the above α ——➤ β change was suggested several months prior to the publication of Phillips and Mumford's paper, by Wilson and Ott (*loc. cit.*), who stated that the transition is probably due to a change in the rotation of the molecules, not involving any change in length; *i.e.*, a change from a vertical rotating (α) form to a vertical non-rotating (β) form. Since, however, Wilson and Ott did not investigate the changes in side spacings which accompany changes in rotation (Müller, *Nature*, 1932, 129, 436; *Proc. Roy. Soc.*, 1932, *A*, 138, 514; see also Malkin, *Trans. Faraday Soc.*, 1933, 29, 977), I have measured the side spacings of the α- and β-forms of C_{15}, C_{17}, and C_{19} alcohols and find, in agreement with the above suggestion, that the β-forms give two main spacings (3·7 and 4·2 Å.), whereas the α-forms give only one (4·2 Å.).

Further, confirmation of rotation in the α-forms of odd alcohols is given by their optical properties. Thus, the α-forms of the above three alcohols are uniaxial, whereas the β-forms are biaxial. These results are in harmony with the observations of Bernal, who found the same difference between the α- and the β-form of the even alcohol, dodecylol (*Z. Krist.*, 1932, 83, 153).—THE UNIVERSITY, BRISTOL. [*Received, March 26th,* 1935.]

161. *Factors modifying the Polarisation of Liquids.*

By FRANK R. GOSS.

IN a discussion (Goss, this vol., p. 502) of the effects of association and the anisotropy of the field on the dielectric polarisation of liquids and certain liquid mixtures, the formulæ developed, when applied to the data for mixtures of nitrobenzene with other liquids, showed that the polarisation coefficients of the solvents were in some cases increased by a term (K) which was considered to arise from the orientation, in the electric field, of the co-ordinate links to which association is attributed. This view was supported by evidence that the abnormal polarisation is most marked in those liquids for which a large measure of association is deduced from their other physical properties.

Association of this nature cannot arise in the vapour state, and in order to test the conclusion that a non-polar liquid may possess a "false" orientation polarisation in the liquid state due to association, although in the vapour state it is undoubtedly non-polar, a careful comparison has been made between benzene and carbon tetrachloride. In the vapour state both these substances have been shown, by McAlpine and Smyth (*J. Amer. Chem. Soc.*, 1933, **55**, 453) and by Sänger (*Physikal. Z.*, 1926, **27**, 556) respectively, to have an electrical polarisation which does not vary with temperature, and hence a dipole moment and orientation polarisation of zero. In the liquid state the electrical polarisation of both these substances is depressed by the anisotropy of the field in accordance with the Raman–Krishnan theory, but it is to be expected that the association effect in benzene would result in the observed depression being less than that required by this theory.

The anisotropy factor for benzene has been given by Krishnan (*Proc. Roy. Soc.*, 1929, *A*, **126**, 155), who calculated that at 20° the observed polarisation of the liquid should be 3·6% lower than the true polarisation P_B as observed for the vapour. This diminution is given by the product of the volume polarisation p_B and the molecular anisotropy factor * A_B, previously defined (Goss, *loc. cit.*), so that

$$[R_L]_\infty = P_B - p_B A_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $[R_L]_\infty$ is the molecular refractivity corrected for dispersion, and $P_B = (n_\infty^2 - 1)/(n_\infty^2 + 2)$: n_∞ is the refractive index calculated from known values of the refractive index n corresponding to wave-lengths λ by an expression similar to that of Sellmeier, viz., $n^2 = n_\infty^2 + k_B/(\lambda^2 - \lambda_B^2)$ (cf. Goss, J., 1933, 1341).

From the experimental data given in Table VI, values of $[R_L]_\infty$ and p_B over the temperature range 10—50° are given for benzene (Table III), and the values of P_B and A_B can be readily calculated by employing expression (1) combined with Krishnan's data for the effect of anisotropy ($p_B A_B/P_B = 0.036$ at 20°); P_B is found to be 26·244 c.c. and is, of course, a constant, but A_B decreases rapidly with temperature, having the value $3·3 - 0·007t + 0·00003t^2$. The molecular refractivity of benzene at infinite wave-length is thus

$$[R_L]_\infty = 26·244 - (3·3 - 0·007t + 0·00003t^2)(n_\infty^2 - 1)/(n_\infty^2 + 2).$$

Numerous attempts have been made to modify the Lorentz–Lorenz expression for molecular refraction in order to obtain a function of the refractive index independent of temperature, one of the most successful being Eykman's empirical expression $(n^2 - 1)M/(n + 0·4)D$ (*Rec. trav. chim.*, 1895, **14**, 185). The only function which can theoretically be independent of temperature is the electron polarisation, $P_B = (n_\infty^2 - 1)(A_B + M/D)/(n_\infty^2 + 2)$, where allowance is made both for the anisotropy of the local field and for dispersion, as the variations of these two factors with temperature are not inter-related. Nevertheless, if the Lorentz–Lorenz formula is corrected by the anisotropy factor A_B alone, it becomes $(n^2 - 1)(A_B + M/D)/(n^2 + 2)$, which, as is shown in the penultimate line of Table I, is nearly independent of temperature and should equal the molecular refraction

* It has been suggested that the use of the term "anisotropy factor" in this sense might lead to confusion owing to the use of the same expression by Kuhn and Braun (*Z. physikal. Chem.*, 1930, *B*, **8**, 445) for the Cotton effect. Its use here, in defining the modification of the polarisation field, would appear, however, to be the more logical and is a reasoned development of the work of Krishnan (*loc. cit.*).

$(n^2 - 1)M/3D$ of the vapour for the same wave-length. A comparison of the values given by the various formulæ which have been proposed, including those of Gladstone and Dale and of Parker and Thompson (J., 1922, 121, 1341), is given in Table I, calculated from the values of n_D and D for benzene given in Table VI.

<div align="center">

TABLE I.

Molecular refraction of liquid benzene.

</div>

t	10°.	20°	30°.	40°.	50°.
$(n_D^2 - 1)M/(n_D^2 + 2) D$ .... Lorentz–Lorenz	26·16	26·19	26·23	26·26	26·29
$(n_D - 1)M/D$ .... Gladstone–Dale	44·58	44·55	44·51	44·49	44·44
$(n_D^2 - 1)M/(n_D + 0·4) D$ .... Eykman	58·59	58·61	58·61	58·61	58·61
$(n_D^2 - 1·15)M/(n_D^2 + 1) D$ .... Parker–Thompson	30·13	30·14	30·16	30·18	30·18
$(n_D^2 - 1)(A_E + M/D)/(n_D^2 + 2)$	27·12	27·13	27·13	27·14	27·15
$(n_\infty^2 - 1)(A_E + M/D)/(n_\infty^2 + 2)$	26·24	26·24	26·24	26·24	26·24

Now, corresponding to expression (1), there is the equation (2) which expresses the electrical polarisation P_2 of a non-polar, non-associating liquid such as carbon tetrachloride, in terms of the true polarisation P_{E+A} as obtained by measurements on the vapour :

$$P_2 = P_{E+A} - pA_{E+A} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where p is the volume polarisation of the liquid $[p = (\varepsilon - 1)/(\varepsilon + 2)]$ and A_{E+A} is the anisotropy factor. The probability that the anisotropy factors for the optical and the electrical field in a non-polar liquid are equal has already been discussed on the basis of existing data (Goss, J., 1933, 1341). The physical constants of carbon tetrachloride have now been redetermined to ensure that the data employed refer to a single sample, and are suitable for substitution in the differentials of equations (1) and (2). Krishnan (*loc. cit.*) has made use of this differentiation, and it is found that

$$- (n_\infty^2 - 1)(n_\infty^2 + 2)/3(dn_\infty^2/dt) = (1 + DA_E/M)/[(dA_E/dt)D/M - (dD/dt)/D] \quad (3)$$

and $\quad - (\varepsilon - 1)(\varepsilon + 2)/3(d\varepsilon/dt) = (1 + DA_{E+A}/M)/[(dA_{E+A}/dt)D/M - (dD/dt)/D] \quad (4)$

These equations provide a very sensitive test of the relationship between the anisotropy factors A_E and A_{E+A}; within the limits of the experimental accuracy attained, the results of the present investigation show (Table II) that for carbon tetrachloride the left-hand sides of (3) and (4) are equal over a range of temperature, and therefore, the right-hand sides being equal, it follows that $A_E = A_{E+A}$, so (2) and (4) may be rewritten

$$P_2 = P_{E+A} - pA_E \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$- (\varepsilon - 1)(\varepsilon + 2)/3(d\varepsilon/dt) = (1 + DA_E/M)/[(dA_E/dt)D/M - (dD/dt)/D] \quad . \quad (6)$$

<div align="center">

TABLE II.

</div>

t	Carbon tetrachloride.					Benzene.				
	10°.	20°.	30°.	40°.	50°.	10°.	20°.	30°.	40°.	50°.
$- (n_\infty^2 - 1)(n_\infty^2 + 2)/3(dn_\infty^2/dt)$	904	881	859	837	815	919	901	883	865	847
$- (\varepsilon - 1)(\varepsilon + 2)/3(d\varepsilon/dt)$	903	880	857	835	813	943	925	906	888	870

For benzene, the left-hand sides of equations (3) and (6) are definitely unequal, and consequently it is possible to calculate from the relationship $(n_\infty^2 - 1)(n_\infty^2 + 2)/3(dn_\infty^2/dt) = (\varepsilon' - 1)(\varepsilon' + 2)/3(d\varepsilon'/dt)$ the dielectric constant ε' which benzene would have if the electrical polarisation were modified solely by the anisotropy of the local field as represented in equation (2). It is found that $\varepsilon' = 2·2960 - 0·00198t$, and the corresponding polarisations P' will give the true value of P_{E+A} since

$$P_{E+A} = P' + pA_E \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The observed polarisation of liquid benzene in an electrical field is greater than P', so $P_2 = P_{E+A} - pA_2 + K$, the term K representing the " false " orientation polarisation previously observed and referred to on p. 727. The values calculated for the polarisation coefficients of benzene are in Table III.

TABLE III.

Polarisation of benzene.

t		10°.	20°.	30°.	40°.	50°.
Optical poln., corr. for distortion	$[R_L]_\infty$	25·311	25·339	25·365	25·389	25·411
Electrical poln., obs.	P_2	26·567	26·604	26·639	26·672	26·703
Electrical poln., corr. for association ...	P'	26·193	26·222	26·249	26·273	26·295
Anisotropy factor	A_R	3·233	3·172	3·117	3·068	3·025
Electron poln. ....:...............	P_E	26·244	26·244	26·244	26·244	26·244
Electron and atom poln.	P_{E+A}	27·172	27·172	27·172	27·172	27·172
Atom poln.	P_A	0·928	0·928	0·928	0·928	0·928
Association term	K	0·374	0·382	0·390	0·399	0·408
Optical anisotropy term	$p_E A_R$	0·932	0·905	0·879	0·855	0·834
Electrical anisotropy term	pA_E	0·979	0·950	0·923	0·899	0·876
Electl. poln., corr. for anisotropy only	P''	27·546	27·554	27·562	27·571	27·579
Optical volume poln.	p_E	0·2884	0·2852	0·2821	0·2788	0·2756
Electrical volume poln.....................	p	0·3027	0·2995	0·2962	0·2929	0·2896

The value of P_{E+A} given by expression (7) is seen to be independent of temperature and is in good agreement with the value of 27·0 c.c. found by McAlpine and Smyth (*loc. cit.*) for the vapour. A value of 26·2 c.c. for the vapour has been recorded by Groves and Sugden (J., 1934, 1094), but this, contrary to theory, is lower than the polarisation of the liquid. If the observed electrical polarisation of liquid benzene is corrected for anisotropy but not for association, the resulting coefficient P'' increases with temperature, and the value (Table III) is considerably higher than that of the vapour.

It is now possible to obtain more accurate values for the atom polarisation than hitherto, since it is evident that a true value is only obtained if allowance is made for association, and if, in addition, the optical and the electrical polarisation are compared under the same physical conditions of state and temperature, *i.e.*, $P_A = P_2 - [R_L]_\infty - K$, where P_2 and $[R_L]_\infty$ are at the same temperature, or, more accurately, $P_A = P_{E+A} - P_E$. The atom polarisation of carbon tetrachloride has been calculated by the former relation, and the data are in Table IV.

TABLE IV.

Polarisation of carbon tetrachloride.

t		10°.	20°.	30°	40°.	50°
Optical poln , corr for distortion	$[R_L]_\infty$	25·986	26·016	26·040	26·058	26·069
Electrical poln , obs	P_2	28·100	28·131	28·157	28·176	28·187
Atom poln	P_A	2·1	2·1	2·1	2·1	2·1

EXPERIMENTAL.

Purification of Materials.—The measurements were made with the samples of benzene and carbon tetrachloride previously described (Goss, *loc. cit.*).

Variation of Physical Properties with Temperature.—The variation of physical properties recorded in Table VI can be reduced in every case to an expression of the form $X = a - bt \pm ct^2$ for $t = 10$—60°. The physical properties of liquid benzene at temperatures lower than 10° do not, however, as Piekara (*Bull. Acad. Polonaise*, 1933, *A*, 305) has shown, conform to an expression of this type. No evidence was obtained in support of the allotropy of liquid benzene reported by Menzies and Lacoss (*Proc. Nat. Acad. Sci.*, 1932, **18**, 144; cf. Deinum, *Rec. trav. chim.*, 1934, **53**, 1061). In some cases more exact data than those here recorded are already available, but in order to obtain values suitable for the calculation of the polarisation coefficients, it is essential that all the necessary measurements should be carried out under standardised conditions on one sample of material. Special care has been taken to obtain accurate values for the *temperature coefficients* of the refractive indices and dielectric constants, since these quantities are involved in the above formulæ. The dielectric constant of benzene has been taken as $2·3221 - 0·00198t$ (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 685; Meyer,

Z. physikal. Chem., 1930, *B*, **8**, 27; Piekara, *loc. cit.*); this value is assumed to be the dielectric constant of the above sample of benzene which was used in calibrating the condenser (see below).

Measurement of Temperature.—Temperatures were measured by thermometers which were from time to time compared with an N.P.L. standard; they were kept constant to the nearest 0·05°, which corresponds with a change of one unit in the fourth place of decimals for the various properties examined.

Density.—This was measured in the usual way with an Ostwald–Sprengel pyknometer, and the liquids were freed from dissolved air by boiling just before measurements were made.

Refractive Index.—A Pulfrich refractometer (Messrs. Bellingham and Stanley, Ltd.) was employed, the temperature control being maintained by water flowing, at the rate of about 500 c.c. per min., from a thermostat of 13 l. capacity, through the jackets enclosing the prism and through the tubular heater, the whole of these being enclosed in a specially constructed heat-insulating jacket of asbestos. The temperature of the out-flowing water was determined by a calibrated thermometer in the heater. Lowry (*J. Sci. Inst.*, 1923, **1**, 16) has shown that any difference between the temperature so recorded and the real temperature of the liquid under examination is, other conditions being uniform, proportional to the difference between the recorded and the room temperature. Two readings were therefore taken with the circulating water at 30°, and the room temperature successively at 20° and 30°. As the readings were identical, it follows that, under the above conditions, the thermometer in the heater accurately records the temperature of the liquid under examination. Readings were taken for the sodium D line and the hydrogen α and β lines, and the refractive indices at infinite wave-length were calculated from these by the formula given on p. 727.

Dielectric Constant.—The apparatus previously described (Goss, *loc. cit.*) was employed with a few modifications; the temperature of the chlorobenzene bath in which the experimental condenser is immersed was maintained within the desired limits (see above) by water circulated at the rate of 500 c.c. per min. through earthed metal tubes from a thermostat of 13 l. capacity. The experimental condenser, which had an air capacity of 182 $\mu\mu$ F, was recalibrated by Piekara's method (*loc. cit.*), according to which readings are first taken when the condenser contains benzene (*E*) and dry air (*F*), the values obtained being given in Table V.

TABLE V.

Calibration of condenser.

t	10°.	20°.	30°.	40°.	50°.	60°.
E ………	404·535	459·915	454·915	450·335	445·77	441·45
F ………	228·00	227·065	226·08	225·215	224·435	223·65

$A = 2\cdot3208 - 0\cdot0019751t$, $B = 1 + 0\cdot159/T$; $C = 47\cdot9 - 0\cdot074t$; $D' = 181\cdot9 - 0\cdot013t$.

TABLE VI.

Experimental data.

	Benzene.						Carbon tetrachloride.					
t	10°.	20°.	30°.	40°.	50°.	60°.	10°.	20°.	30°.	40°.	50°.	60°.
D	—	0·87880	0·86811	0·85744	0·84674	0·83605	—	1·59418	1·57447	1·55492	1·53574	1·51564
ϵ	2·3023	2·2825	2·2627	2·2429	2·2231	2·2033	2·2540	2·2345	2·2146	2·1951	2·1741	2·1544
n_α	1·5035	1·4971	1·4907	1·4842	1·4778	—	1·4639	1·4580	1·4520	1·4460	1·4398	—
n_D	1·5079	1·5015	1·4950	1·4885	1·4820	—	1·4661	1·4602	1·4542	1·4482	1·4420	—
n_β	1·5204	1·5138	1·5073	1·5006	1·4941	—	1·4737	1·4677	1·4616	1·4555	1·4493	—

Benzene.

$D = 0\cdot90019 - 0\cdot001069t$; $\epsilon = 2\cdot3221 - 0\cdot00198t$; $n^2 = 2\cdot2344 - 0\cdot00186t + (0\cdot0165 - 0\cdot00002t)/(\nu^2 - 0\cdot066)$.

Carbon tetrachloride.

$D = 163372 - 0\cdot00199t + 0\cdot0000005t^2$; $\epsilon = 2\cdot2738 - 0\cdot00196t - 0\cdot0000005t^2$; $n^2 = 2\cdot145 - 0\cdot00170t - 0\cdot0000005t^2 + (0\cdot00603 - 0\cdot000006t)/(\nu^2 - 0\cdot11)$.

The liquid under investigation is then introduced and the new capacity (*G*) measured; its dielectric constant $\epsilon = (G - C)B/D'$, where *B* is the dielectric constant of dry air, $C = (E - AF)/(1 - A)$, where *A* is the dielectric constant of benzene (relative to air), and $D' = F - C$. It will be noted that D' is the true air capacity of the experimental condenser, and *C* its capacity to earth.

SUMMARY.

1. The molecular anisotropy factors A_B and A_{B+A}, arising respectively from the local asymmetry of the optical and the electrical polarisation field, in liquids, have in earlier work been assumed to be equal. This equality is now proved for carbon tetrachloride.

2. The " false " orientation polarisation of liquid benzene, previously noted and attributed to the presence of co-ordinate links, is measured over a range of temperature.

3. Several expressions for molecular refraction are compared from the point of view of their independence of temperature.

THE UNIVERSITY, LEEDS.

162. *The Planar Structure of Quadricovalent Cupric Compounds.*

By E. G. COX and K. C. WEBSTER.

DURING the recent investigations on the compounds of salicylaldoxime with nickel, palladium, and platinum (this vol., p. 459), the copper derivative (I) was prepared, and a preliminary investigation suggested that, although this compound is not isomorphous with either of the others, yet the molecule in this case also might possess a planar structure. Moreover, the planar arrangement around the copper of the four chlorine atoms in the six-co-ordinated complex [$CuCl_4,2H_2O$]'' (Hendricks and Dickinson, *J. Amer. Chem. Soc.*, 1927, **49**, 2149), and of four water molecules in $CuSO_4,5H_2O$ (Beevers and Lipson, *Proc. Roy. Soc.*, 1934, **146**, *A*, 570) suggested that, if suitable four-co-ordinated compounds were examined, a planar structure would be found. We have therefore studied by means of X-rays some other chelated compounds of bivalent copper, *viz.*, the copper salts of acetylacetone (II; $R_1 = R_2 = CH_3$, $R_3 = H$), of benzoylacetone (II; $R_1 = C_6H_5$, $R_2 = CH_3$, $R_3 = H$), of dipropionylmethane (II; $R_1 = R_2 = C_2H_5$, $R_3 = H$), and of 3-chloroacetylacetone (II; $R_1 = R_2 = CH_3$, $R_3 = Cl$).
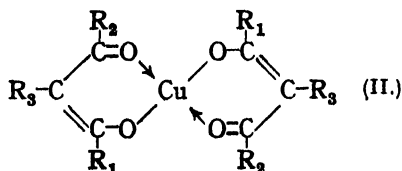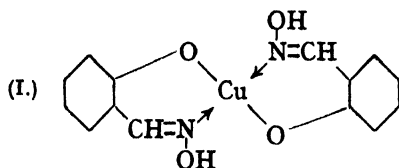
These investigations have definitely established that in the crystalline state these quadricovalent compounds of bivalent copper possess a planar structure. On account of the large number of parameters involved, a complete determination of the crystalline structure of any one of these compounds would be a very laborious undertaking; it has been possible, however, to demonstrate their planar configuration conclusively by means of (*a*) space-group considerations, (*b*) cell dimensions, and (*c*) optical properties. In view of the importance of these results, it is desirable to consider briefly the validity of the evidence under these heads.

(*a*) *Space-group Considerations.*—All the substances concerned (with the possible exception of the chloro-compound, which was not studied so thoroughly as the others) are monoclinic, and careful tests by means of liquid air (Martin, *Phil. Mag.*, 1931, **22**, 519) showed them to be non-pyroelectric, so that they belong to the prismatic class. The space-group was determined in each case by careful examination of numerous oscillation photographs taken with long exposures, special search being made for reflexions from such planes as the odd orders of (010), which were of particular importance in this respect. The compounds with acetylacetone and benzoylacetone gave identical results; the space-group was found to be C_{2h}^5 ($P2_1/n$), so that, since the cell contains only two molecules, each molecule must possess a centre of symmetry. In both these compounds, therefore, the copper atom and its four surrounding oxygen atoms are coplanar. It should be emphasised that in a case of this kind, where the symmetry is established by failure to find certain

reflexions after careful search, although it is conceivable that still more exhaustive search might reveal very weak " forbidden " lines, yet the main conclusions would be unaffected, since such weak reflexions would merely indicate the very slightest divergence from perfect centro-symmetry. It may also be pointed out that the halvings for this particular space-group are different from those of any other in the monoclinic system; the results are independent of those of the pyroelectric tests, although the two are in agreement.

The salicylaldoxime derivative has the symmetry of the space-group C_{2h}^5 ($P2_1/n$) with four molecules in the cell, but an additional set of halvings indicates that the molecule of this compound also possesses a centre of symmetry. The space-group of the dipropionyl-methane compound is C_{2h}^6 ($A2/a$), and as far as symmetry requirements are concerned, the molecule may have either a two-fold axis or a centre of symmetry; the former, however, is excluded by the cell dimensions.

(b) *Cell Dimensions.*—It is well established that the distance apart of carbon atoms in neighbouring molecules of crystalline organic compounds is approximately 3·7 Å.U. (see, *e.g.*, Robertson, Report of International Conference on Physics, 1934, II, 46, where the smallest carbon–carbon distance recorded is 3·4 Å.U.). From these values, a simple calculation shows that if, in the crystal of copper acetylacetonate, the disposition of the Cu–O bonds were tetrahedral, the distance apart of copper atoms in neighbouring molecules would probably be about 5·3 Å.U., and certainly not less than 4·8 Å.U. In the substituted acetylacetone compounds the distance would probably be somewhat greater. On the other hand, with a planar distribution of valencies, the distance apart of copper atoms in neighbouring molecules might be anything from about 3·7 Å.U. upwards, according to the arrangement of the molecules. Actually, for each of the four diketone compounds examined, one of the cell dimensions (which must be the distance apart of copper atoms in different molecules) is less than 4·8 Å.U.; this constitutes strong support for the conclusion drawn from the space-group results, *viz.*, that the molecules concerned are planar. As might be anticipated, the short axes of these substances are directions of very pronounced acicular growth.

(c) *Optical Properties.*—A molecule in which the two chelate groups are in planes at right angles (*i.e.*, in which the valencies of the central atom are tetrahedral) will possess a much smaller optical anisotropy than a molecule in which the chelate groups are coplanar; the latter alternative is therefore supported by the fact that at least two of the compounds studied have extremely high birefringence. It should be observed that, although the arrangement of highly anisotropic molecules in the crystal may be such as to produce low birefringence, yet no crystalline structure can give rise to high birefringence when the molecules themselves are not greatly anisotropic.

Since the compounds in which a planar distribution has been established appear to be in no way exceptional, it is reasonable to infer that the planar arrangement is normal for four-co-ordinated compounds of bivalent copper. This result, which confirms the view expressed by Werner, is not in accordance with the conclusions of Mills and Gotts (*J.*, 1926, 3121), who obtained a strychnine salt of cupribenzoylpyruvic acid showing a small but definite mutarotation. These authors, however, were unable to remove the strychnine, and admit that the case for optical activity rests only on analogy with the behaviour of the brucine salt of the corresponding beryllium complex. Since there is no doubt as to the tetrahedral configuration of beryllium, it seems that this analogy is false, and that the observed results of Mills and Gotts were due to some cause other than a tetrahedral copper atom.

The present result is interesting also from a theoretical point of view. According to Pauling (*J. Amer. Chem. Soc.*, 1931, 53, 1391), a planar configuration is to be expected when s, p, and d electrons are involved in the valency bonds; it is possible, therefore, that bivalent copper possesses a complete 3_3 sub-group of ten electrons, some being shared, instead of an incomplete group of nine as is usually supposed. This would involve one unpaired electron in the fourth principal quantum level, giving rise to a paramagnetic moment of the same order as that actually observed (Sugden, *J.*, 1932, 161).

EXPERIMENTAL.

The X-ray investigations were carried out by means of single-crystal rotation and oscillation photographs, using $Cu_{K\alpha}$ radiation, the probable accuracy of the cell dimensions being about $\frac{1}{2}\%$. Refractive indices were determined by immersion methods to 0·01.

Copper Disalicylaldoxime.—This was prepared by the addition of a slight excess of aqueous salicylaldoxime to a solution of cupric chloride made alkaline with caustic soda and then acidified with acetic acid. The dried product was recrystallised from chloroform (Found : Cu, 18·87; N, 8·4. Calc. for $CuC_{14}H_{12}O_4N_2$: Cu, 18·94; N, 8·4%).

The molecular weight was determined by the cryoscopic method in naphthalene and the following results obtained ($M = 336$) : for $c = 3·336$ and 1·914 g./1000 g., $\Delta t = 0·070°$ and 0·040° respectively, whence $M = 327, 329$.

The crystals were found to be monoclinic holohedral combinations of $a\{100\}$, $p\{011\}$, $o\{111\}$, and $O\{11\bar{1}\}$; tabular on a. X-Ray measurements give $a = 27·61$, $b = 6·00$, $c = 7·86$ Å.U., $\beta = 98°$ 13'. With four molecules to the unit cell, d(calc.) = 1·72 g./c.c. (Found : 1·72).

Abnormal spacings : $\{0k0\}$ absent when k is odd, all $\{h0l\}$ planes halved. These halvings are those of the space-group C_{2h}^5 ($P2_1/a$) [$\{010\}$ halved and $\{h0l\}$ halved for h odd] together with an additional halving [$\{h0l\}$ halved for l odd], indicating a further glide parallel to the c-axis. A consideration of the symmetry of this space-group shows that this additional halving (with four molecules in the cell) is only possible if each molecule possesses a centre of symmetry.

Optical properties : $\alpha = 1·55$, $\beta = 1·73$, $\gamma > 1·91$, $\gamma - \alpha > 0·36$. The plane of the optic axes is (010) and the acute bisectrix is nearly perpendicular to (100). Optic axial angle large; optic sign positive. These results indicate flat molecules arranged with their longest direction approximately parallel to the a-axis; the length of the latter is in good agreement with this.

Copper Acetylacetonate.—The crystals examined were from a highly purified specimen prepared by Morgan and co-workers. They are blue monoclinic needles with fractured ends (Found : Cu, 24·10; C, 45·9; H, 5·4. Calc. for $CuC_{10}H_{14}O_4$: Cu, 24·30; C, 45·8; H, 5·4%).

Forms observed were $a\{100\}$, $r\{101\}$, and $R\{10\bar{1}\}$; pronounced elongation along [b]. From X-ray measurements : $a = 11·24$, $b = 4·68$, $c = 10·24$ Å.U., $\beta = 92°$ 00'. With two molecules in the unit cell, d (calc.) = 1·58 g./c.c. (Found : 1·57).

Reflexions not occurring : $\{h0l\}$ when $h + l$ is odd, $\{0k0\}$ when k is odd. The space-group is therefore C_{2h}^5 ($P2_1/n$), and each molecule in the crystal has a centre of symmetry.

Refractive indices : α (parallel to [b]) = 1·59, $\gamma \geqslant 1·69$.

Copper Benzoylacetonate.—Prepared by the addition of cupric acetate solution to an alcoholic solution of benzoylacetone and recrystallisation from hot alcohol (Found : C, 62·4; H, 4·4. Calc. for $CuC_{20}H_{18}O_4$: C, 62·2; H, 4·7%).

The crystals are long needles with fractured ends, and were found to be monoclinic prisms elongated along [c]. Forms observed were $a\{100\}$ and $m\{110\}$. X-Ray measurements give $a = 18·19$, $b = 10·44$, $c = 4·43$ Å.U., $\beta = 96°$ 58'. For two molecules in the cell, d (calc.) = 1·53 g./c.c. (Found : 1·53).

Reflexions not occurring : $\{h0l\}$ when $h + l$ is odd, $\{0k0\}$ when k is odd. Hence the space-group is C_{2h}^5 ($P2_1/n$), and the molecule has a centre of symmetry.

Refractive indices : α (inclined at 21° to [c]) = 1·57, $\gamma > 1·78$. These indices, in agreement with the X-ray results, indicate flat molecules more or less parallel to (001).

Copper Salt of Dipropionylmethane.—These crystals, also from a highly purified sample prepared by Morgan and co-workers, were deep blue monoclinic needles elongated along [b], owing to the ends being fractured, the only forms observed were $a\{100\}$ and $c\{001\}$. X-Ray measurements give $a = 19·44$, $b = 4·63$, $c = 16·72$ Å.U., $\beta = 89°$ 33'. Density calculated for two molecules per unit cell = 1·40 g./c.c. (Found : 1·39).

Abnormal spacings : $\{hkl\}$ absent when $k + l$ is odd, all $\{h0l\}$ halved. The space-group is therefore C_{2h}^6 ($A2/a$), whence the molecule may have either a two-fold axis or a centre of symmetry; the small value of [b], however, excludes the possibility of the former.

Birefringence greater than 0·07. Strong dichroism.

Copper 3-Chloroacetylacetonate.—Thin needles showing inclined extinction. Only the needle axis of this compound was measured, and found to be 4·78 Å.U. Birefringence greater than 0·10.

163. *A New Alkaloid from the Bark of* Holarrhena Antidysenterica.

By D. H. Peacock and J. C. Chowdhury.

The bark of *Holarrhena antidysenterica* is used in Burma as a remedy for dysentery and as a febrifuge under the name of lettôk. An examination of the bark derived from local sources has shown the existence of another alkaloid in addition to those already described by other workers. The alkaloid content of the bark varied between 1·36 and 1·2%. The alkaloids were extracted by three methods : (1) cold dilute hydrochloric acid, (2) cold alcohol, (3) hot alcohol. A second extraction with alcoholic ammonia (Siddiqui and Pillay, *J. Indian Chem. Soc.*, 1933, **10**, 673) yielded an extra 0·1—0·2% of alkaloids. The crude alkaloids were isolated from the solutions in the usual way and an alkaloid giving a hydrochloride soluble in water but sparingly soluble in hydrochloric acid was found. This base, $C_{17}H_{25}O_2N$, was purified through the *hydriodide*, m.p. 256° (decomp.), and obtained as a light brown powder, m. p. 350—352°. It does not appear to be identical with any of the alkaloids previously described as present in the bark of *Holarrhena antidysenterica* (conessine, $C_{24}H_{40}N_2$, m. p. 125°, Haines, *Pharm. J.*, 1865, ii, **6**, 432 ; conessimine, $C_{20}H_{38}N_2$, m. p. 100° ; holarrhine, $C_{30}H_{38}O_3N_2$, m. p. 240° ; holarrhimine, $C_{21}H_{36}ON_2$, m. p. 183°, Siddiqui and Pillay, *J. Indian Chem. Soc.*, 1932, **9**, 553 ; *iso*conessimine, $C_{23}H_{38}N_2$, m. p. 92° ; conimine, $C_{22}H_{36}N_2$, m. p. 130°, *idem, ibid.*, 1934, **11**, 283 ; holarrhemine, $C_{24}H_{38}ON_2$, m. p. 197°, Pyman, J., 1919, **115**, 63 ; kurchine, $C_{23}H_{38}N_2$, m. p. 75° ; kurchicine, $C_{20}H_{36}ON_2$, m. p. 175°, Ghosh and Ghosh, *J. Indian Chem. Soc.*, 1928, **5**, 477 ; norconessine, $C_{23}H_{38}N_2$, b. p. 240°/0·7 mm., R. D. Haworth, J., 1932, 631 ; conessidine, $C_{21}H_{32}N_2$, m. p. 123° ; conkurchine, $C_{22}H_{32}N_2$, m. p. 153° ; kurchenine, $C_{21}H_{32}O_2N_2$, m. p. 335—336°, Bertho, Schuckmann, and Schönberger, *Ber.*, 1933, **66**, 786) and the name *lettocine* is suggested for it. It appears to be a tertiary base and to contain no hydroxyl groups. The amount present in the bark is less than 0·1% and we are accumulating a sufficient quantity for further examination. The aqueous mother-liquor after the extraction of alkaloids by chloroform was tested for quaternary ammonium bases, but none were found.

No alkaloids were found in the latex of the tree. Alcoholic extraction yielded two colourless crystalline solids of the resinol type which are under investigation.

Experimental.

1580 G. of the powdered bark were extracted with 7 l. of 1% hydrochloric acid and the solution was made faintly acid to Congo-red with 10% aqueous ammonia and extracted with chloroform. The aqueous solution was basified with aqueous ammonia and the precipitated alkaloids were extracted in chloroform, dried, and recovered (14·5 g.). Alternatively, 4200 g. of the bark were extracted with 6 l. of rectified spirit, the solution distilled under reduced pressure, the residue treated with 1% hydrochloric acid, and the alkaloids isolated as before (35 g.). The crude bases (49·5 g.) were treated with 700 c.c. of 5% hydrochloric acid ; the insoluble hydrochloride was collected and dissolved in water (300 c.c.), and the solution made alkaline with 10% aqueous ammonia and extracted four times with chloroform. The chloroform extract was shaken with 5% hydrochloric acid, and the aqueous solution added to the above solution of hydrochlorides, but the precipitated hydrochloride was filtered off and dissolved in water. This solution was basified with ammonia and extracted with chloroform, and the alkaloid recovered (5·7 g.) was dissolved in rectified spirit (20 c.c.), and 10% hydriodic acid added until the solution was acid to Congo-red. The dark brown *hydriodide* (5·9 g.) was crystallised twice from hot rectified spirit and obtained as a yellowish-brown, microcrystalline powder, m.p. 256° (decomp.) [Found : I, 31·9 (Carius), 32·8, 32·6. $C_{17}H_{25}O_2N,HI$ requires I, 31·5%].

The hydriodide, triturated with aqueous ammonia, gave *lettocine*. This separated from chloroform–light petroleum as a light brown, microcrystalline powder, m.p. 350—352° [Found : C, 74·4, 74·9 ; H, 8·9, 8·9 ; N, 5·1, 5·2 ; M (ebullioscopic in chloroform), 298, 313, 292, 284, 295. $C_{17}H_{25}O_2N$ requires C, 74·2 ; H, 9·1 ; N, 5·1 ; M, 275]. The base is soluble in alcohol and chloroform, sparingly soluble in ether and light petroleum. The picrate, crystallised from hot absolute alcohol, had m. p. 198°. The oxalate was soluble in water and sparingly soluble in ethyl alcohol. The base was recovered unchanged after some hours' boiling with acetic anhydride.

The base was (1) dissolved in aqueous oxalic acid and extracted four times with ether, and (2) made into a paste with lead hydroxide and extracted with alcohol; in both cases it was recovered unchanged in m. p. Crystallisation from ethyl alcohol–acetone also left the m. p. unchanged.

The Methiodide.—The base (0·3 g.) was boiled for 3 hours with methyl alcohol (5 c.c.) and methyl iodide (1 c.c.). The solvent was distilled, and the dark brown residue crystallised from hot methyl alcohol; m. p. 235° (Found : I, 30·5. $C_{18}H_{26}O_2NI$ requires I, 30·6%).

Our thanks are due to the Forestry Department, Burma, for the collection of the bark and latex used and its identification, and to the University of Rangoon for a grant.

University College, Rangoon.

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164. *The Action of Selenium on Compounds containing Angular Methyl Groups.*

By George R. Clemo and Haydn G. Dickenson.

The wide use of selenium dehydrogenation (Diels, *Ber.*, 1927, **60**, 2323) in elucidating the skeletal structures of many naturally occurring organic compounds, especially terpenes and sterols, renders it important to investigate the limitations of the method. It is drastic, and a typical case of a misleading result due to a structural change is the production of chrysene from cholesterol, which is now known to embody a *cyclo*pentenophenanthrene skeleton (I) and not that of chrysene. The latter is presumably produced by a ring enlargement involving the angular methyl group.

(I.)   (II.)   (III.)   (IV)
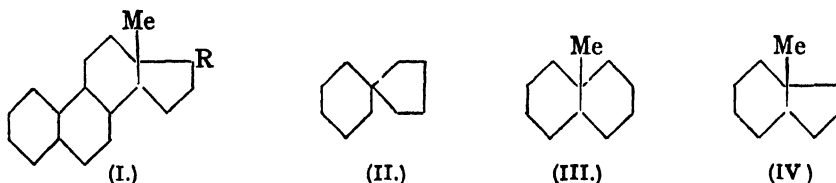
In the dehydrogenation of the sterols there is also produced a hydrocarbon, $C_{18}H_{16}$, known as Diels's hydrocarbon. This has now been identified with 3'-methyl-1 : 2-*cyclo*pentenophenanthrene, which presumably arises from the loss of R, and the wandering of the methyl group from the angular to the 3'-position in the *cyclo*pentenophenanthrene skeleton.

Clemo and Ormston (J., 1933, 352) showed that ring structural changes did occur, as they obtained naphthalene by the dehydrogenation of *cyclo*hexane*spirocyclo*pentane (II) with selenium at 280—330°, and it was proposed to continue this work by studying the selenium dehydrogenation of compounds containing angular methyl groups, in particular, 9-methyldecalin (III) (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1154) and 8-methylhydrindane (IV). 1 : 1 : 6-Trimethyltetralin (V) also has been investigated.

(V)   (VI.)   (VII)
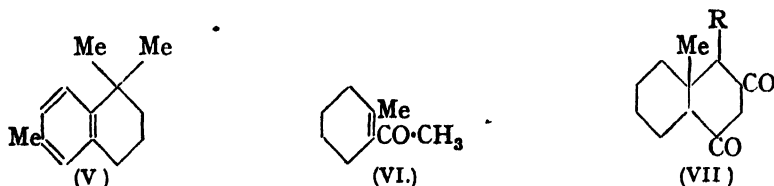
Ruzicka's synthesis of (III) was as follows : 2-acetyl-1-methyl-Δ^1-*cyclo*hexene (VI) was condensed with sodiomalonic ester to give the diketo-ester (VII) (R = CO_2Et), which, on hydrolysis, gave the diketone (VII, R = H). This, on reduction by Clemmensen's method, gave 9-methyl-*trans*-decalin (III). No proof of the structure of the diketone (VII, R = H) was advanced save that it was oxidised to a dibasic acid, the methyl ester

of which gave the analytical results required for that of (IX). There is therefore a possibility that the double bond in (VI) might have migrated before the Michael addition to give (VIII) instead of (VII, R = CO$_2$Et), which would ultimately yield 1-methyl-*trans*-decalin.


(VIII.)   (IX.)   (X.)
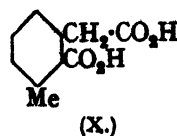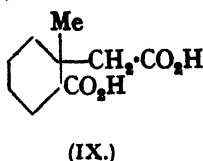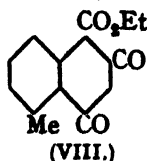
The synthesis has been repeated and the compounds (VII, R = H and CO$_2$Et), hitherto isolated as impure oils, have been obtained crystalline, m. p. 127—129° and 129—130° respectively. They give correct analytical results if special precautions are taken, but are apt to give a low value for carbon, possibly due to a tendency for the angular methyl group to escape as methane.

The diketone, whether derived from (VII) or (VIII), is a strong acid and is remarkable in giving no evidence for the presence of reactive keto- or methylene groups when treated with piperonal, semicarbazide, or *o*-aminobenzaldehyde. It is readily oxidised by hypobromite to the *cis*-form of the dicarboxylic acid (IX) or (X), but permanganate gives only a very poor yield of a different acid. In an attempt to decide between formulæ (IX) and (X) by heating the *cis*-acid with selenium, whereby toluene and *m*-xylene respectively might be expected to result, the acid was recovered as the stable anhydride.

The hydrocarbon was then obtained as described by Ruzicka and had a characteristic odour, quite distinct from that of 1-methyldecalin. All attempts to dehydrogenate it failed, it being recovered unchanged after being heated for 100 hours with selenium at 280—330°. A very small amount of material boiled slightly higher and gave the analytical results required for C$_{10}$H$_{16}$. It was thought to be 9 : 10-octalin, but the characteristic dibromide could not be obtained. Dehydrogenation was then attempted by the method of Ehrenstein (*Ber.*, 1931, **64**, 1137) with a platinum catalyst and, though decalin and 1-methyldecalin were converted readily into naphthalene and 1-methylnaphthalene respectively in this way, the hydrocarbon in question was unattacked. Sulphur (which led to much decomposition), sulphur and selenium, and selenium dioxide were also ineffective.

When the diketone was treated with phosphorus pentachloride in chloroform, it gave a *dichloro*-compound (XI) which, when heated with selenium, gave 1-methylnaphthalene. The conclusion drawn from this rather surprising result is that the diketone is (VII, R = H) and gives 9-methyl-*trans*-decalin as claimed by Ruzicka.

Whether the methyl group migrates into the unsaturated ring during the preparation of the dichloro-compound or in the subsequent heating is not known, as the various migrations furnish inconclusive evidence on the point. These migrations are similar to the conversion of 3 · 5-dichloro-1 : 1-dimethyl-Δ$^{2\cdot4}$-dihydrobenzene (XII) (Crossley and Le Sueur, J., 1902, **81**, 1536) into 3 : 5-dichloro-*o*-xylene (XIII).

(XI.)   (XII.)   (XIII.)   (XIV)
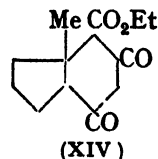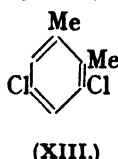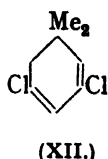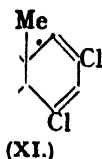
2-Acetyl-1-methyl-Δ^1-*cyclo*pentene condenses readily with sodiomalonic ester to give the diketohydrindane derivative (XIV), which, on hydrolysis and reduction, gives 8-*methyl*-*trans*-*hydrindane* (IV). The yields are better than in the case of 9-methyldecalin. The hydrocarbon has a terpene-like odour and, as in the previous case, all attempts to dehydrogenate it failed, the original substance being recovered in each case and no evidence found for its conversion into either naphthalene or methylindene.

The diketone obtained from (XIV) gave a dichloro-compound as in the previous case, but this, on treatment with selenium, gave no recognisable products, only a minute amount of a non-picrate-forming oil being isolated.

The hydrocarbon (V) obtained by ring closure of α-ionone (Tiemann and Kruger, *Ber.*, 1893, **26**, 2683) was heated with selenium at 290—310° and gave a good yield of 1 : 6-dimethylnaphthalene (compare also Ruzicka and Rudolph, *Helv. Chim. Acta*, 1927, **10**, 916), there being no evidence of a migration from the 1-position.

EXPERIMENTAL.

9-*Methyldecalin.*—The diketo-ester (VII, R = CO_2Et) was prepared as described by Ruzicka (*loc. cit.*) except that the ethereal extract of the reaction mixture was extracted twice with sodium carbonate solution. The combined carbonate extracts on acidification yielded the diketo-ester as a pale yellow oil, which solidified after 1—2 hours (yield, 50%). It was recrystallised from dilute alcohol, giving small colourless prisms, m. p. 127—129° [Found : C, 66·2; H, 8·2; *M* (Rast), 256. Calc. for $C_{14}H_{20}O_4$: C, 66·7; H, 7·9%; *M*, 252].

The above ester (30 g.) was hydrolysed by boiling with 20% alcoholic potash (150 c.c.) on the water-bath for 8 hours. The product was diluted with water, the alcohol removed, the residue acidified (hydrochloric acid), and the 2 : 4-diketo-9-methyldecalin extracted with ether. On distillation it was obtained as a faintly yellow, glassy resin (17 g.), b. p. 155°/0·3 mm. This solidified with difficulty and then crystallised from petroleum–benzene in minute colourless prisms, m. p. 129—130° (Found : C, 72·7; H, 8·9. Calc. for $C_{11}H_{16}O_2$: C, 73·3; H, 8·9%). A molecular-weight determination by the method of Rast indicated considerable association.

9-Methyldecalin was obtained by reducing the above diketone as described by Ruzicka (*loc. cit.*).

Attempted Dehydrogenation of 9-*Methyldecalin.*—The hydrocarbon (0·9 g.) was heated with selenium (4 g.) at 260—280° for 12 hours and at 300—340° for a further 36 hours. The residue consisted of the original hydrocarbon (0·6 g.) and a higher-boiling fraction (0·1 g.), b. p. 82—84°/18 mm. This was treated with picric acid (0·15 g.) in alcohol (1 c.c.), but only picric acid (0·075 g.) crystallised, even after concentration of the solution. The recovered hydrocarbon was again treated with selenium for a further 48 hours, but only a small amount of the liquid, b. p. 82—84°/18 mm., was isolated (Found : C, 88·1; H, 11·9. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%).

Dichloro-compound (XI).—The diketone (above) was treated with 1½ times the theoretical quantity of phosphorus pentachloride in chloroform. After 2—3 hours' refluxing, the excess of the pentachloride was decomposed with water, the chloroform removed, and the product fractionated. The *dichloro*-compound boiled at 150—155°/13 mm. (Found : C, 60·4; H, 6·2. $C_{11}H_{14}Cl_2$ requires C, 60·8; H, 6·45%).

Dehydrogenation of the Dichloro-compound.—The compound (2 g.) with selenium (4 g.) was heated at 280—300° for 60 hours. The residue was extracted with chloroform, the solution filtered (charcoal), the solvent removed, and the oil dissolved in light petroleum and again filtered from selenium. On distillation over sodium it yielded a hydrocarbon (0·8 g.), b. p. approx. 110°/12 mm., which gave a bright yellow picrate, m. p. 140—141°, not depressed by admixture with 1-methylnaphthalene picrate (Found : C, 54·7; H, 3·75. Calc. for $C_{17}H_{13}O_7N_3$: C, 55·0; H, 3·5%).

2-*Carboxy*-1-*methylcyclohexane*-1-*acetic Acid* (IX).—The *cis*-acid was obtained by oxidation of the diketone with hypobromite (Ruzicka; *loc. cit.*). It crystallised well from water in small prisms, m. p. 172—173° (Found : C, 60·2; H, 8·25. Calc. for $C_{10}H_{16}O_4$: C, 60·0; H, 8·0%).

Attempted Dehydrogenation of the cis-*Acid.*—The acid (1·6 g.) was heated with selenium in a flask with a sealed-on water-cooled condenser at 280—300° for 24 hours and at 330° for a further 36 hours. The residue consisted of unchanged acid (as the anhydride) and a trace of a liquid, b. p. approx. 110°/760 mm. When the ester was used in place of the acid, it was recovered unchanged.

8-*Methylhydrindane* (IV).—2-Acetyl-1-methyl-Δ^1-*cyclo*pentene was obtained, in rather poor yield, either by the method of Perkin and Marshall (*J.*, 1890, **57**, 242) or by the method used above starting from methyl-Δ^1-*cyclo*pentene. The latter method is superior if the ketone is to be made in quantity; it is then obtained as an oil, b. p. 191°/760 mm.

Ethyl 2 : 4-diketo-8-methylhydrindane-1-carboxylate was obtained in a similar manner to the decalin compound (above.) The yield is better (50—60%), but the diketo-ester has been obtained only as a yellowish glassy resin, b. p. 150—160°/0·3 mm. It was hydrolysed by refluxing with alcoholic potash as above, and after distillation 2 : 4-*diketo*-8-*methylhydrindane* (b. p. 143°/0·3 mm.) gradually solidified; it crystallised from petroleum–ether in colourless prisms, m. p. 91—92° (Found : C, 72·9; H, 8·7. $C_{10}H_{14}O_2$ requires C, 72·4; H, 8·45%). The

diketone (4 g.) was refluxed with amalgamated zinc (40 g.) and concentrated hydrochloric acid (40 c.c.) for 14 hours, fresh acid being added at intervals. The product was extracted with ether, washed with alkali and water, and fractionated over potassium, pure 8-*methylhydrindane* being obtained as a colourless liquid (1 g.), b. p. 159—160°/760 mm. (Found : C, 87·5; H, 12·7. $C_{10}H_{18}$ requires C, 87·0; H, 13·0%).

Dichloro-compound from 2 : 4-*Diketo-*8-*methylhydrindane.*—This diketone yielded, in exactly the same way as the previous diketone (VII, R = H), a *dichloro-*compound, which was isolated as an oil, b. p. 109—110°/12 mm. (Found: C, 59·0; H, 6·3. $C_{10}H_{12}Cl_2$ requires C, 59·1; H, 5·9%).

Attempted Dehydrogenation of the Above Dichloro-compound.—The substance (1 g.) was heated with selenium (2 g.) at 280—300° for 24 hours. There was much decomposition, and extraction of the product yielded a very small amount of oil which did not give a picrate or condense with piperonal as would be expected had it been an indene derivative.

1 : 1 : 6-*Trimethyltetralin.*—This compound was obtained as an oil, b. p. 130°/30 mm., as described in the literature. It was dehydrogenated with selenium in the usual way and gave a 60% yield of 1 : 6-dimethylnaphthalene (picrate, orange needles, m. p. and mixed m. p. 110—111°).

165. *Syntheses and Molecular Complexes in the Phenazine Series.* Part II.

By GEORGE R. CLEMO and HENRY MCILWAIN.

THOUGH Briegleb (*Z. physikal. Chem.*, 1932, B, **16**, 249) has classified the types of linkage which can lead theoretically to molecular compounds, it is not easy to discriminate between these in practice, and there are few such compounds for which a single formula is generally accepted. We have suggested (Part I; J., 1934, 1991) a formula for the phenazhydrins formed from the phenazine and its reduced form involving the co-ordination of the nitrogen atom of the former with the imino-hydrogen atom of the latter. Though the conception of —H— may receive a different interpretation on current wave-mechanical views, there is chemical and physical evidence (see especially Sidgwick, *Ann. Reports,* 1934, 40) indicating that hydrogen has peculiar combining powers when joined to an atom of considerable " residual affinity " and that it can form a bridge between two such centres.

We have attempted to find the centres participating in complex formation in the phenazine series by varying the components. There appear to be two distinct types of molecular compound in the phenazine series : (1) The true phenazhydrins, formed between a phenazine and a 9 : 10-dihydrophenazine; these are much less soluble than their components in such solvents as alcohol or petrol, are green to purple, and form green dihydrochlorides. (2) Phenazine–primary or secondary aromatic base complexes; these are more soluble than the phenazhydrins, are orange-red, and do not give complex hydrochlorides.

A reason for the complex hydrochlorides being specific of the phenazhydrins proper is to be seen in Michaelis's formulation of these salts (*J. Amer. Chem. Soc.,* 1933, **55**, 1481),
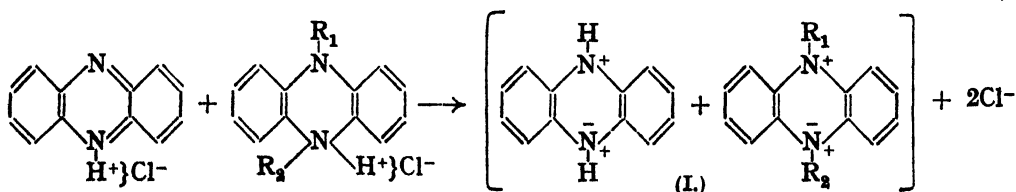
which he suggests owe their stability and colour to their existence as ions (I, $R_1 = R_2 = H$) (the monohydrochloride of phenazine is known; the *dihydrophenazine salt,* not previously

described, has been found also to be a monohydrochloride). Evidence supporting this formulation has been obtained from a study of the methylated dihydrophenazines. *N*-Methyldihydrophenazine was made by the method of Hantzsch (*Ber.*, 1916, **49**, 513) through phenazine methosulphate; but *NN'*-dimethyldihydrophenazine could not be made similarly, as phenazine forms only a monomethosulphate. An intermolecular Ullmann reaction with *o*-chloro-*N*-methylaniline, which would have yielded the required compound, did not take place. It has been prepared, however, from *NN'*-dimethyl-*o*-phenylene-diamine and *cyclo*hexane-1 : 2-dione by condensation and oxidation.

Neither of these methylated dihydrophenazines yields a complex with phenazine, thus supporting the formula II (Part I) for the phenazhydrins, but both form complex hydro-chlorides, which can be written as (I : *a*, R$_1$ = H, R$_2$ = CH$_3$; *b*, R$_1$ = R$_2$ = CH$_3$).

Further evidence that the *N*-hydrogen atoms perform a function in complex formation which an *N*-methyl group cannot is furnished by the second class of phenazine molecular compounds : phenazine forms with diphenylamine a loosely-bound orange-coloured *complex* in the molecular ratio of 1 : 2; no combination was found with methyldiphenylamine. Phenazine and *o*-phenylenediamine form a 1 : 1-*complex*, but *NN'*-dimethyl-*o*-phenylene-diamine does not combine, a result unexpected till one considers that mutual repulsion or steric interference of the two methyl groups will orient them, and consequently the *N*-hydrogen atoms, on opposite sides of the plane of the benzene ring.

The nature of the complexes formed between phenazine and the various phenylene-diamines indicates that an approach in space of the participating N and H atoms is neces-sary : with the *o*- and *m*-compounds, 1 : 1 complexes are formed, but under the same conditions the *p*-diamine yields a 1 : 2-*complex*. This supports the previously recorded observations on heteronuclear phenazhydrins (Part I). It is noteworthy that Buehler and collaborators (*J. Amer. Chem. Soc.*, 1932, **54**, 2398), from a physical study of the phenol-amines, concludes that these compounds also are bound co-ordinately.

1 : 2 : 3 : 4-Tetrahydrophenazine, which contains the quinoxaline nucleus, has not been found to combine with dihydrophenazine; nor will 1 : 2 : 3 . 4 : 9 : 10 : 11 : 12-*octahydro-phenazine*, which contains two cyclic imino-groups between one benzenoid and one reduced ring, combine with phenazine or its tetrahydro-compounds. No complex is formed between the octahydro- and the tetrahydro-phenazine, nor between these compounds and diphenylamine. This indicates that the benzene nuclei also play some specific part, sterically or electromerically, in phenazhydrin formation.

Neither carbazole nor acridine gives complexes comparable with the phenazhydrins, but the latter does yield equimolecular compounds with such bases as diphenylamine (Blum, *Ber.*, 1929, **62**, 885).

Kögl and collaborators (*Annalen*, 1932, **497**, 266) consider that the reduced nucleus in the phenazhydrin chlororaphin is in the 10 : 13-dihydro-form (II). Their evidence—that chlororaphin has three active hydrogen atoms in its molecule, phenazine none, dihydro-phenazine two, the amide of phenazine-α-carboxylic acid one, and hence the amide of 9 : 10-dihydrophenazine-α-carboxylic acid three, whereas in the form (II) it would have two such atoms, making with that of the amide of phenazine-α-carboxylic acid the observed three—can be criticised on two grounds.

(II.)   (III.)
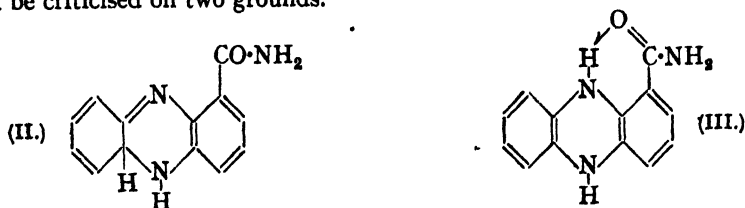
We have found that chlororaphin gives in the amyl ether of a Zerewitinov estimation a yellow solution, taken by Kögl as signifying dissociation; he is thus estimating the active hydrogen atoms of a mixture of the amide of phenazine-α-carboxylic acid and its dihydro-form, which implies that the latter has two such atoms. We suggest that this discrepancy

from the computed value is due to the co-ordination indicated in formula (III) and not to a radically different ring structure. Such co-ordination also explains the relative stability to oxidation exhibited by chlororaphin in comparison with the corresponding complex from the β-amide, the dihydro-form of which cannot so co-ordinate. Phenazine-β-carboxylic acid has been made in a similar manner to the α-acid (compare Part I) from 2-methylphenazine, and the latter from the two new 2-*methyl*-1 : 2 : 3 : 4- and -5 : 6 : 7 : 8-*tetrahydrophenazines* described in the experimental part.

It was found that the β-amide would not yield the corresponding phenazhydrin by a simple zinc reduction as will the α-compound, and that when prepared from its 9 : 10-dihydro-form it oxidises in air at room temperature, whereas chlororaphin remains unchanged.

<div align="center">EXPERIMENTAL.</div>

Phenazine–N-*methyldihydrophenazine Dihydrochloride.*—To a solution of *N*-methyldihydrophenazine (0·1 g.) and phenazine (0·1 g.) in the least amount of alcohol, saturated alcoholic hydrogen chloride (1 c.c.) was added; the *salt* precipitated from the dark green solution by ether crystallised from alcohol in fine green needles, m. p. 225° (approx., decomp.) (Found : Cl, 15·7, 16·0. $C_{13}H_9N_2,C_{12}H_{10}N_2,2HCl$ requires Cl, 15·8%). The salt yields with alkalis a mixture of its constituent bases, which form no compound in the usual solvents.

NN'-*Dimethyl*-2 : 3 : 9 : 10-*tetrahydrophenazine.*—*cyclo*Hexane-1 : 2-dione (5·6 g.), *NN'*-dimethyl-*o*-phenylenediamine (6·8 g.), and concentrated hydrochloric acid (20 c.c.) in water (60 c.c.) were rapidly brought to boiling, refluxed for 5 minutes, and quickly cooled, the hydrochloride of the condensation product was filtered off and dissolved in water, excess of sodium hydroxide added, and the *base* collected, washed with water, and crystallised from alcohol, forming colourless plates (2·2 g.), m. p. 78° (Found : C, 79·2; H, 7·85. $C_{14}H_{16}N_2$ requires C, 79·25; H, 7·6%).

NN'-*Dimethyl*-9 : 10-*dihydrophenazine.*—*cyclo*Hexane-1 : 2-dione (1 g.), *NN'*-dimethyl-*o*-phenylenediamine (1·2 g.), sodium acetate (2 g.), and glacial acetic acid (5 c.c.) were refluxed for 40 minutes and poured into water and the mixture was made alkaline and extracted with ether. From the resinous ethereal concentrates, a *solid* (0·15 g.) was separated with difficulty, and crystallised from benzene or absolute alcohol in almost colourless prisms, m. p. 153° (Found : C, 80·1; H, 6·65; N, 13·2. $C_{14}H_{14}N_2$ requires C, 80·0; H, 6·7; N, 13·3%).

This substance was also produced when solutions of the above tetrahydro-compound were exposed to the air for some days, or an acetic acid solution was warmed in the open for ¼ hour; the bulk of the material was, however, converted into a resin, and the usual dehydrogenating agents gave no better yield. The colourless hydrochloride of *NN'*-dimethyldihydrophenazine turned green on exposure to air or on the addition of oxidising agents; when an oxidised solution was made alkaline and extracted with light petroleum, phenazine was obtained. A similar oxidative demethylation was observed with *N*-methyldihydrophenazine.

Phenazine–NN'-*dimethyl*-9 : 10-*dihydrophenazine Dihydrochloride.*—The *salt* was obtained, in the same way as its monomethyl analogue above, in dark green needles, m. p. 225—230° (decomp.) (Found : Cl, 15·6. $C_{13}H_8N_2,C_{14}H_{14}N_2,2HCl$ requires Cl, 15·35%).

Phenazine–*Base Complexes.*—In each case, warm saturated solutions of the components, in various molecular ratios, were mixed in suitable solvents (light petroleum, ether, alcohol, acetone, benzene, or mixtures of these) and cooled or concentrated till the material crystallised, combined or otherwise. The following results were obtained :

(a) *Phenazine*–o-*phenylenediamine*, from alcohol, gave orange prisms, m. p. 153° (Found : C, 75·8; H, 5·4. $C_{12}H_8N_2,C_6H_8N_2$ requires C, 75·0; H, 5·55%).

(b) *Phenazine*–m-*phenylenediamine*, from alcohol, gave orange prisms, m. p. 143° (Found : C, 75·8; H, 5·6. $C_{12}H_8N_2,C_6H_8N_2$ requires C, 75·0; H, 5·55%).

(c) *Phenazine*–p-*phenylenediamine* crystallised in red prisms, m. p. 133°, from alcohol–light petroleum (Found : C, 73·4; H, 6·4. $C_{12}H_8N_2,2C_6H_8N_2$ requires C, 72·7; H, 6·1%).

(d) *Phenazine*–*diphenylamine* crystallised from alcohol in orange plates, m.p. 57—58° (Found : C, 83·7; H, 6·1. $C_{12}H_8N_2,2C_{12}H_{11}N$ requires C, 83·4; H, 5·8%).

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydrophenazine.*—1 : 2 : 3 : 4-Tetrahydrophenazine (0·5 g.), sodium amalgam (15 g. of 4%), and alcohol (10 c.c.) were refluxed for 24 hours, the solution evaporated to crystallisation point, and the *product* recrystallised from alcohol, forming colourless plates (0·25 g.), m. p. 150°, an acid solution of which gave a deep purple coloration with ferric chloride (Found : C, 76·8; H, 8·75. $C_{12}H_{16}N_2$ requires C, 76·6; H, 8·5%).

2-Methyl-1 : 2 : 3 : 4-tetrahydrophenazine.—1-Methylcyclohexane-3 : 4-dione (Wallach, *Annalen*, 1916, 414, 321; 1924, 437, 162) (13 g.), o-phenylenediamine (11 g.), sodium acetate (15 g.), and glacial acetic acid (30 c.c.) were refluxed for 2 hours and poured into water and the solution was made alkaline and extracted with ether. The bulk of the product distilled at 144—148°/ 0·1 mm. (15 g.) and on redistillation at 147°/0·1 mm. gave a bright yellow *oil* (Found : C, 78·5; H, 6·9. $C_{13}H_{14}N_2$ requires C, 78·8; H, 7·1%).

2-Methyl-5 : 6 : 7 : 8-tetrahydrophenazine.—p-Methyl-o-phenylenediamine (3·6 g.), cyclohexane-1 : 2-dione (3·3 g.), sodium acetate (5 g.), and glacial acetic acid (15 c.c.) were refluxed for 2 hours and the solution was poured into water, made alkaline, and extracted with ether. The *product* (5·5 g.) crystallised from light petroleum in yellow prisms, m. p. 78° (Found : C, 78·9; H, 7·5. $C_{13}H_{14}N_2$ requires C, 78·8; H, 7·1%).

2-Methylphenazine.—The above tetrahydro-compounds (2 g.) were separately refluxed with iodine (5·2 g.) in glacial acetic acid (10 c.c.) for 8 hours, the mixture cooled and made alkaline with dilute sodium hydroxide solution, and 2-methylphenazine distilled in superheated steam. It crystallised from light petroleum in light yellow needles (1 g.), m. p. 117° (Found : C, 80·6, H, 4·9. Calc. for $C_{13}H_{10}N_2$: C, 80·4; H, 5·15%).

Phenazine-2-carboxylic Acid.—2-Methylphenazine (1 g.), chromic acid (1·5 g.), and glacial acetic acid were refluxed for ¼ hour, the product was poured into water and made alkaline, and the unchanged material extracted with ether; the aqueous solution was made acid, and the product extracted and crystallised from acetone, giving yellow needles (0·1 g.), m p. 292° (Found : C, 69·7, H, 3·9. Calc. for $C_{13}H_8O_2N_2$. C, 69·7, H, 3·6%). The amide and its phenazhydrin were made by the method of Kogl and collaborators (*loc. cit.*).

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166.   The Friedel and Crafts Reaction in the Carbazole Series.

By S. G. P. PLANT, (MISS) K. M. ROGERS, and S. B. C. WILLIAMS.

AN examination of the few recorded instances of the use of simple acid halides in Friedel and Crafts reactions in the carbazole series suggests that there may be a profound difference in the course adopted when the reaction is applied to 9-acylcarbazoles on the one hand and carbazoles with a free >NH group on the other. In the latter class carbazole itself appears to undergo substitution in both the 3- and the 6-position, even in the presence of a limited amount of the acid halide, and in 3-substituted carbazoles the process is completed by the introduction of a single acyl group in the 6-position (Plant and Tomlinson, J., 1932, 2188). The reaction with 9-acylcarbazoles appears to involve substitution of a single acyl radical into the 2-position (Borsche and Feise, *Ber.*, 1907, 40, 378; I. G. Farbenind. Akt.-Ges., D.R.-P. 555,312; Plant and Williams, J., 1934, 1142). The main object of the present work has been to investigate the validity of this generalisation.

When carbazole was treated with acetyl bromide (two molecular proportions) and aluminium chloride in carbon disulphide, a diacetylcarbazole (m. p. 232°) was obtained. The use of restricted amounts of acetyl bromide in efforts to prepare a monoacetyl derivative resulted in the recovery of considerable quantities of carbazole. Attempts to identify this product have involved the synthesis along the usual lines of 5 : 4'-diacetyl-1-phenyl-benzotriazole (I) and 5-acetyl-1-phenyl-4'-ethylbenzotriazole, but efforts to convert these
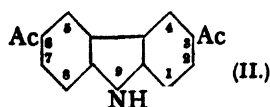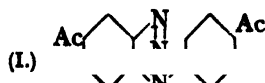
substances into carbazole derivatives with loss of nitrogen were unsuccessful. The latter would have given 3-acetyl-6-ethylcarbazole, but it was hoped to identify the 3 : 6-diethyl-

3 C

carbazole obtained on reduction with the product obtained by reducing the diacetyl compound of m. p. 232°.

Ultimately 3 : 6-*diethylcarbazole* was synthesised by condensing 4-ethyl*cyclo*hexanone with *p*-ethylphenylhydrazine, converting the hydrazone by Fischer's reaction into 3 : 6-*diethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, and oxidising the latter with sulphur in boiling quinoline. It proved to be identical with the product obtained by applying Clemmensen's method of reduction to the diacetyl compound mentioned above, and it therefore follows that the Friedel and Crafts reaction with carbazole and acetyl bromide leads to 3 : 6-*diacetylcarbazole* (II).

The generalisation has been further tested by treating, first, 3-benzoylcarbazole with acetyl bromide and aluminium chloride, and, secondly, 3-acetylcarbazole with benzoyl chloride and aluminium chloride. The products were identical, from which it follows that they must be 3-*benzoyl-6-acetylcarbazole*.

In order to study the reaction with the 9-alkylcarbazoles, 9-methylcarbazole was treated with acetyl bromide and aluminium chloride in carbon disulphide; the product was 3 : 6-*diacetyl-9-methylcarbazole*, identical with the substance obtained by methylating the 3 : 6-diacetylcarbazole described above. The use of only one molecular proportion of acetyl bromide also resulted in the formation of a considerable quantity of the diacetyl compound, there being no indication of the presence of any appreciable amount of a mono-acetyl derivative.

In the conversion of 9-benzoylcarbazole by benzoyl chloride and aluminium chloride into 3 : 6-dibenzoylcarbazole (Plant and Tomlinson, *loc. cit.*) migration of the benzoyl group to the 3-position, which is known to be induced by aluminium chloride, must precede substitution. In several attempts to repeat the preparation of 3 : 6-dibenzoylcarbazole in this way, however, the main product has been the isomeric 2 : 9-*dibenzoylcarbazole*, formed in accordance with the generalisation mentioned above. It was found to be easily hydrolysed to 2-*benzoylcarbazole*, the constitution of which was proved by the fact that it gave carbazole-2-carboxylic acid on fusion with potassium hydroxide. These discordant observations in this particular reaction have not been traced to any obvious variations in conditions, and are probably due to very minor changes in the quality of the materials used.

9-Acetylcarbazole has been converted by a similar process into 2-*benzoyl-9-acetylcarbazole*, which has also yielded 2-benzoylcarbazole on hydrolysis. This preparation and characterisation of 2-benzoylcarbazole is of interest in view of a statement (D.R.-P. 555,312) to the effect that 2-benzoylcarbazole results as a compound melting above 360° from the benzoylation of 9-acetylcarbazole in carbon tetrachloride with aluminium chloride and a little iodine, and subsequent hydrolysis. In the absence of further details it is impossible to say what this product can be, but it is apparently not 2-benzoylcarbazole.

EXPERIMENTAL.

3 : 6-*Diacetylcarbazole*.—A mixture of carbazole (6 g.), carbon disulphide (50 c.c.), and pulverised aluminium chloride (10 g.) was treated with acetyl bromide (9 g.), the whole refluxed for an hour, and the solvent allowed to evaporate. The 3 : 6-*diacetylcarbazole* obtained by treating the residue with ice–dilute hydrochloric acid was isolated in colourless prisms, m. p. 232°, after two crystallisations from alcohol (Found : C, 76·4; H, 5·5. $C_{16}H_{13}O_2N$ requires C, 76·5; H, 5·2%).

When a solution of this substance (1 g.) in acetone (20 c.c.) was shaken with aqueous potassium hydroxide (3 g. of 35%) and acetyl chloride (3 c.c.) for 10 minutes and then diluted with water, 3 : 6 : 9-*triacetylcarbazole*, colourless needles, m. p. 220°, from acetic acid, was obtained (Found : C, 73·7; H, 5·2. $C_{18}H_{15}O_3N$ requires C, 73·7; H, 5·1%). By a similar process, using methyl sulphate instead of acetyl chloride, 3 : 6-*diacetyl-9-methylcarbazole*, colourless prisms, m. p. 192°, from acetic acid, was prepared (Found : C, 76·8; H, 5·6. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·7%).

5 : 4'-*Diacetyl-1-phenylbenzotriazole*.—A mixture of *p*-aminoacetophenone (5·3 g.), 4-bromo-3-nitroacetophenone (9 g.), and potassium carbonate (4·5 g.) with a little copper powder was heated in an oil-bath at 150° and stirred until frothing ceased and a pasty mass resulted. The product was extracted several times with alcohol, and the united extracts boiled for 10 minutes

with charcoal. *2-Nitro-4 : 4'-diacetyldiphenylamine*, red prisms, m. p. 177°, from methyl alcohol, was precipitated in poor yield when the filtered solution was poured into dilute hydrochloric acid (Found : C, 63·7; H, 4·9; N, 9·8. $C_{16}H_{14}O_4N_2$ requires C, 64·4; H, 4·7; N, 9·4%). A solution of this compound (1·1 g.) in glacial acetic acid (15 c.c.) was boiled with stannous chloride (5 g.) and concentrated hydrochloric acid (12 c.c.) for 10 minutes, cooled, and made alkaline with concentrated aqueous sodium hydroxide. The resulting amine, which was extracted with ether and recovered by evaporation of the dried solution, was dissolved in warm acetic acid (10 c.c.) and treated with sodium nitrite (0·3 g. in a little water). The addition of more water completed the precipitation of 5 : 4'-*diacetyl-1-phenylbenzotriazole*, colourless plates, m. p. 224°, from alcohol (Found : N, 15·1. $C_{16}H_{12}O_2N_3$ requires N, 15·1%).

5-Acetyl-1-phenyl-4'-ethylbenzotriazole.—Prepared from *p*-aminoethylbenzene by a process similar to that described above for 2-nitro-4 : 4'-diacetyldiphenylamine, but with the omission of the copper powder, 2-*nitro-4-acetyl-4'-ethyldiphenylamine* separated from methyl alcohol in red prisms, m. p. 85° (Found : N, 10·0. $C_{16}H_{16}O_3N_2$ requires N, 9·9%). The nitro-compound was converted as before into the corresponding amine, yellow prisms, m. p. 106°, from alcohol, and then into 5-*acetyl-1-phenyl-4'-ethylbenzotriazole*, colourless needles, m. p. 143°, from alcohol (Found : N, 16·2. $C_{16}H_{15}ON_3$ requires N, 15·9%).

3 : 6-Diethylcarbazole and its Synthesis.—Granulated zinc (200 g.) was left in aqueous mercuric chloride (400 c.c. of 5%) for an hour, the solution was poured away, and 3 : 6-diacetylcarbazole (3 g.) added. The mixture was shaken with concentrated hydrochloric acid (50 c.c.) for a few minutes and left over-night. After the addition of anisole (5 c.c.) and more concentrated hydrochloric acid (20 c.c.), the whole was refluxed for 12 hours, and the product extracted with ether. The extract was washed with dilute hydrochloric acid, water, and aqueous sodium carbonate, then dried and evaporated, the anisole being removed from the residue by steam distillation. The product was taken up in ether and purified by distillation under reduced pressure; the distillate solidified, and, on crystallisation from acetic acid, 3 : 6-*diethylcarbazole* was obtained in colourless plates, m. p. 119° (Found : C, 85·5; H, 7·4; N, 6·3. $C_{16}H_{17}N$ requires C, 86·1; H, 7·6; N, 6·3%).

p-Ethylphenol, b. p. 212—215° (compare Beilstein and Kuhlberg, *Annalen*, 1870, **156**, 206), prepared from sodium *p*-ethylbenzenesulphonate (Sempotowski, *Ber.*, 1889, **22**, 2662) by fusion with sodium hydroxide, was reduced to 4-ethyl*cyclo*hexanol, b. p. 194—196° (compare von Braun, Mannes, and Reuter, *Ber.*, 1933, **66**, 1499), by passing its vapour together with hydrogen slowly over nickel on pumice at 220°, a certain amount of the unchanged phenol being recovered from the product by extraction with alkali. 4-Ethyl*cyclo*hexanone (5·5 g., b. p. 192—194°; compare von Braun, Mannes, and Reuter, *loc. cit.*), obtained from the ethyl-*cyclo*hexanol as described by Baeyer (*Annalen*, 1894, **278**, 100) for *cyclo*hexanone, was warmed on the steam-bath for a few minutes with *p*-ethylphenylhydrazine (7 g.; see Plant and Williams, *loc. cit.*), and the product boiled for 10 minutes with water (135 c.c.) and concentrated sulphuric acid (15 c.c.). The 3 : 6-*diethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, colourless prisms (5 g.), m. p. 87—88°, from methyl alcohol, which separated as an oil and solidified on cooling (Found . N, 6·4. $C_{16}H_{21}N$ requires N, 6·2%), was boiled (4·35 g.) with sulphur (1·25 g.) in pure quinoline (30 c.c.) for ¼ hour. The product obtained when the resulting solution was poured (cold) on ice–dilute hydrochloric acid was extracted with ether, and the extract dried and evaporated. After the solid residue had been distilled under reduced pressure with a small quantity of iron filings, 3 : 6-diethylcarbazole, identified by mixed m. p. with the substance described above, was obtained; it was isolated in colourless plates, m. p. 117—119°, after crystallisation from acetic acid and then methyl alcohol.

3-Benzoyl-6-acetylcarbazole.—Further experience of the method described by Plant and Williams (*loc. cit.*) for converting 9-acetylcarbazole into 3-acetylcarbazole by heating with aluminium chloride has shown that the procedure is not always entirely satisfactory and on several occasions the reaction has proved to be more complex than the simple isomeric change. It has now been found that the process is very much more reliable when carried out in nitrobenzene. A solution of 9-acetylcarbazole (14 g.) in nitrobenzene (120 c.c.) was treated with aluminium chloride (10 g.), warmed to 120°, and kept at that temperature with occasional shaking for 15 minutes. The whole was poured, when cold, into dilute hydrochloric acid, and the nitrobenzene removed in steam. The residue was boiled in alcohol with charcoal, and the product precipitated from the filtered solution by pouring into dilute hydrochloric acid. When this was crystallised from toluene, reasonably pure 3-acetylcarbazole (5·6 g.), m. p. 162° after softening from 157°, was obtained.

A solution of 3-acetylcarbazole (1·5 g.), aluminium chloride (2 g.), and benzoyl chloride (2 g.)

in nitrobenzene (50 c.c.) was kept at room temperature for a day. The product, isolated as above, was boiled in acetone with charcoal, and 3-*benzoyl-6-acetylcarbazole*, grey prisms, m. p. 210°, after being recrystallised from toluene and then twice from acetic acid, was isolated after filtration by precipitation with dilute hydrochloric acid (Found : C, 80·6; H, 4·5. $C_{21}H_{15}O_2N$ requires C, 80·5; H, 4·8%). The same substance (mixed m. p.) was also obtained when the reactants were refluxed in carbon disulphide for an hour.

Aluminium chloride (1·3 g.) and then acetyl bromide (1·5 c.c.) were added to 3-benzoyl-carbazole (1·3 g.; Plant and Tomlinson, *loc. cit.*) in carbon disulphide (30 c.c.), the mixture was refluxed for 6 hours, the solvent allowed to evaporate, and the residue treated with ice–dilute hydrochloric acid. After the whole had been warmed on the steam-bath for a few minutes, the aqueous liquid was removed by decantation, and the sticky residue purified by boiling in alcohol (170 c.c.) with charcoal for 10 minutes. The 3-benzoyl-6-acetylcarbazole which was recovered from the solution separated in pale green prisms, m. p. 209—210°, after crystallisation from acetic acid and then alcohol, and was identified (mixed m. p.) with the compound described above.

3 : 6-*Diacetyl-9-methylcarbazole.*—Prepared from 9-methylcarbazole by a process similar to that described for 3 : 6-diacetylcarbazole, 3 : 6-diacetyl-9-methylcarbazole was purified by crystallisation from alcohol and then acetic acid, and identified by mixed m. p. with the product mentioned above.

2-*Benzoylcarbazole and its Derivatives.*—9-Benzoylcarbazole (5 g., prepared as described by Mazzara, *Ber.*, 1891, **24**, 278) was refluxed for 4 hours in carbon disulphide (30 c.c.) with benzoyl chloride (3 c.c.) and aluminium chloride (15 g.), the solvent was allowed to evaporate, and the residue treated with ice–dilute hydrochloric acid. When the product was crystallised from alcohol (about 300 c.c.), 2 : 9-*dibenzoylcarbazole*, colourless prisms, m. p. 140—142°, from toluene, was obtained (Found : N, 3·7. $C_{26}H_{17}O_2N$ requires N, 3·7%). By a similar procedure 2-*benzoyl-9-acetylcarbazole*, pale brown needles, m. p. 136—137°, from alcohol, was prepared from 9-acetylcarbazole (Found : N, 4·3. $C_{21}H_{15}O_2N$ requires N, 4·5%).

Both of these substances were hydrolysed by refluxing with aqueous–alcoholic potassium hydroxide for an hour, 2-*benzoylcarbazole*, greenish-yellow plates, m. p. 163°, from glacial acetic acid, being precipitated from the resulting solution by the addition of water (Found : C, 83·9; H, 4·9; N, 5·3. $C_{19}H_{13}ON$ requires C, 84·1; H, 4·8; N, 5·2%). This compound was re-benzoylated by heating with benzoyl chloride at 160—170° for 2 hours, and re-acetylated by refluxing for 2 hours with acetic anhydride containing a trace of sulphuric acid, the products being identified with the substances described above by mixed m. p.

2-Benzoylcarbazole (1·5 g.) was added gradually with stirring to a molten mixture of potassium hydroxide (15 g.) and water (0·75 g.). After the cold residue had been dissolved in water, the addition of sulphuric acid to the filtered solution precipitated carbazole-2-carboxylic acid, colourless prisms, m. p. 320—322°, after crystallisation from aqueous alcohol. This compound was identified by mixed m. p. with an authentic specimen (Plant and Williams, *loc. cit.*) and by conversion into its ethyl ester, m. p. 184°.

167. *Leuco-anthocyanins and Leuco-anthocyanidins. Part I. The Isolation of Peltogynol and its Molecular Structure.*

By (MRS.) G. M. ROBINSON and ROBERT ROBINSON.

THE discussions on the problem of the origin of anthocyanins in the plant have been much obscured in the past by the arbitrary assumption that the chromogens (Palladin's respiratory prochromogens; *Biochem. Z.*, 1909, **18**, 151) are the flavones and flavonols or their glycosides. This was a natural suggestion in 1911 (Wheldale, *J. Genetics*, **1**, 133), but it is not supported by any physiological evidence or by a statistical comparison of the constitutions of congeneric pyrones and pyrylium salts. Indeed, when the chemical relations of these groups became clear as the result of the work of Willstätter on the anthocyanins, the flavone-chromogen obsession was so potent that the acceptable hypothesis of anthocyanin formation by oxidation was discarded by many authors and in some quarters it was maintained that the pigments owe their formation to the reduction of γ-pyrones such as apigenin and quercetin or their glycosides.

Doubtless the details of the oxidase theory of Keeble and Armstrong (*Proc. Roy. Soc.*, 1912, *B*, **85**, 214; *J. Genetics*, 1912, **2**, 277; cf. Keeble, Armstrong, and Jones, *Proc. Roy. Soc.*, 1913, *B*, **86**, 308) require adjustment in the light of present knowledge, but in general terms it is surely in better harmony with the whole of the circumstances of anthocyanin formation than the view attributing a predominant rôle to reduction. Even the experiments *in vitro* cannot be logically interpreted in favour of the reduction hypothesis. The flavones can only be reduced to flavylium salts by metals in strongly acidic media and the yields are very poor; thus no close analogy with the assumed reduction *in vivo* has been provided (Everest, Willstätter, Combes, Shibata *et alii*).

The occurrence in flowers and fruits of colourless substances affording anthocyanin-like pigments on treatment with acids has been frequently noticed, but the significance of these observations has not been fully recognised and the pigments have often been dismissed as "phlobaphenes," a term which in respect of its precision may be classed with "humic acid."

Laborde (*Compt. rend. Acad. Sci.*, 1908, **146**, 1411; **147**, 753, 993) found that unripe green or red grapes contain colourless chromogens which are converted into pigment on heating with dilute hydrochloric acid; Malvezin (*ibid.*, 1908, **147**, 384) showed that the same chromogen developed colour on heating with water at 85°, but only in the presence of air. Dezani (*Staz. sper. agr. Ital., Modena*, 1910, **48**, 428), Tswett (*Biochem. Z.*, 1913, **58**, 225; formaldehyde or acetaldehyde used in addition to hydrochloric acid), Rosenheim (*Biochem. J.*, 1920, **14**, 178), Jonesco (*Compt. rend. Acad. Sci.*, 1921, **173**, 1006; 1922, **175**, 592), and Kozlowski (*ibid.*, 1921, **173**, 855) have also observed the formation of pigments of anthocyanidin-like nature from colourless or pale yellow chromogens without the use of a reducing agent.

Rosenheim (*loc. cit.*) prepared a white amorphous powder of glycosidic nature from the unripe berries of purple grapes or from ripe white grapes and stated that anthocyanidin could be obtained from it by the action of hydrochloric acid in the absence of oxygen. He proposed the expression "leuco-anthocyanin" for the new group of natural products. No indication of the nature of the anthocyanidin obtained from the leuco-anthocyanins was forthcoming in any of the work cited above.

The present authors (*Biochem. J.*, 1933, **27**, 206) have investigated the distribution of leuco-anthocyanins in various parts of plants and have applied a series of qualitative but characteristic tests to the identification of the anthocyanidins produced from the chromogenic material.

The leuco-anthocyanins were thus found to be of widespread occurrence in the vegetable kingdom; the majority of them yielded cyanidin on treatment with hot hydrochloric acid. Curiously enough, the leuco-anthocyanin of white grapes yielded cyanidin whereas the pigment of purple grapes, namely, oenin, is a malvidin glucoside; we had, however, already found that the skins of a red South African grape contained a cyanidin monoglycoside (*Biochem. J.*, 1932, **26**, 1663).

The whole subject appeared so nebulous and yet of such fundamental interest that a careful investigation of particular cases was urgently required.

The leuco-anthocyanins are divided roughly into three classes: (a) those that are insoluble in water and the usual organic solvents, or give only colloidal solutions; (b) those readily soluble in water and not extracted from the solution by means of ethyl acetate; (c) those capable of extraction from aqueous solution by means of ethyl acetate. Probably class (b) consists of relatively simple glycosides or diglycosides, whereas members of class (c) are sugar-free and should be regarded as leuco-anthocyanidins. We directed our attention in the first place to an example in class (c), although the anthocyanidin obtained in this case was clearly not identical with any known aglucone of a plant pigment.

The heartwoods of *Peltogyne porphyrocardia*, *P. pubescens*, and *Copaifera pubiflora* are light brown when freshly cut, but acquire a characteristic purplish-red colour on exposure to light and air (hence the expression "purpleheart"). Aqueous extracts of the saw-dust contain the substance responsible for this property, and on heating such solutions after the addition of hydrochloric acid, a relatively large amount of an anthocyanidin is readily produced. This peltogynidin rather closely resembles a 5-*O*-substituted cyanidin in its

properties, but the acid solutions are a little brighter and more blue-toned red. A full description of this and related flavylium salts is reserved for a future communication. The leuco-anthocyanidin can be isolated by extraction of aqueous solutions with ethyl acetate following a procedure described in the Experimental section. The colourless crystalline substance is named *peltogynol*; it has the composition $C_{16}H_{14}O_6$ and furnishes crystalline *tetra-acetyl*, *tetrabenzoyl*, and *tetra-anisoyl* derivatives; the substance is dextro-rotatory.

On methylation by means of aqueous sodium hydroxide and methyl sulphate, a characteristic *tetramethyl* ether was obtained, but on some occasions this was mixed with a *trimethyl* ether, the two substances being readily separable. It was noticed that the trimethyl ether was produced when the methyl sulphate was in excess and the product had been kept for some hours in contact with the acid solution. Actually the trimethyl ether could be prepared from the pure tetramethyl ether by hydrolysis with hydrochloric acid under mild conditions. The trimethyl ether is insoluble in aqueous alkalis and gives no ferric reaction in alcoholic solution; it is therefore non-phenolic and obviously the fourth methyl group must be associated with a semi-acetal structure of methylglucoside type. This was confirmed by the behaviour of the tetramethyl ether, which was recovered unchanged after treatment with an excess of ethylmagnesium bromide in benzene–ether solution. On the other hand peltogynol itself furnishes a 2 : 4-*dinitrophenylhydrazone*.

Important confirmation of our view of the composition of peltogynol and *O*-tetra-acetylpeltogynol was provided by the optical and *X*-ray crystallographic examination of the substances. This was very kindly undertaken by Miss D. Crowfoot, and her report shows clearly the great value of the new methods for the determination of the molecular weights. Peltogynol and its derivatives showed abnormal cryoscopic behaviour in camphor.

When peltogynol is heated with nitric acid, the combined oxidation and nitration that ensues results in the formation of 2 : 4 : 6-trinitroresorcinol (styphnic acid); on the other hand, the *O*-trimethylpeltogynol afforded 4 : 5-dinitroveratrole. Only traces of the latter were obtained, but on oxidation of the trimethyl ether with potassium permanganate considerable quantities of *m*-hemipinic acid could be isolated. A second product of this degradation was *trimethylpeltogynic acid*, $C_{15}H_8O_2(OMe)_3 \cdot CO_2H$ [or $C_{15}H_{10}O_2(OMe)_3 \cdot CO_2H$], which retains the capacity to furnish a red flavylium salt on oxidation in the presence of acid.

These facts show that peltogynol contains a resorcinol and a catechol nucleus and that the catechol nucleus is 4 : 5-disubstituted, one of the substituting groups being $CH_2 \cdot OH$ or CHO. The very close similarity of the peltogynidin salts to cyanidin chloride being taken into consideration, it is evident that the skeletons (I) and (II) must be considered. The hydroxyl in the resorcinol nucleus cannot be in the alternative position 5 of the benzopyran ring on account of the fluorescence properties exhibited by methylated peltogynidin salts; the 5-methoxy-flavylium salts are non-fluorescent. Similarly the alkali-colour reaction of peltogynidin speaks for a close analogy with fisetinidin.
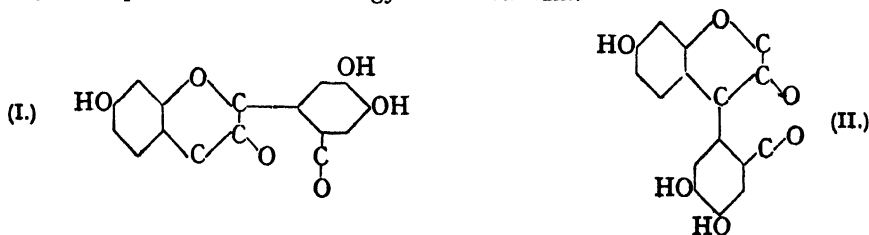
Here the *X*-ray evidence favoured (I), as Miss Crowfoot found it difficult to arrange models based on (II) according to the usual stereochemical assumptions in such a way as to include four molecules per unit cell. Furthermore a pyrylium salt with highly characteristic properties is obtainable from trimethyl or tetramethyl peltogynol, and what appears to be the same substance can be synthesised from fisetinidin chloride tetramethyl ether by condensation with formaldehyde in the presence of concentrated sulphuric acid. The formal

identification of the two specimens is not yet quite complete owing to the difficulties caused by traces of impurities. On the basis of (I), the complete formula for peltogynol should be (III; R, R' = H) or (IV, in semiacetal-type configuration).
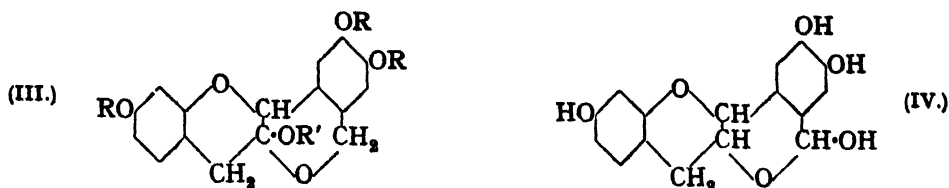
However, (IV) should be no more readily convertible into a flavylium salt than is catechin, whereas (III) represents a true potential leuco-anthocyanidin, the state of oxidation being that of a dihydroflavylium salt. There is, of course, a marked contrast between the behaviour of catechin and peltogynol and their derivatives in respect of the relative ease of conversion into flavylium salts; in the former case the transformation can only be accomplished under special conditions (Appel and Robinson, this vol., p. 426), whereas in the latter case the leuco-anthocyanidin nature of the substance is its most obvious characteristic.

The formula (III) fits all the facts hitherto ascertained and, provisionally accepting it, we may note that, as in the case of cyanomaclurin (see following paper), the dihydroanthocyanidin state of oxidation is stabilised by the ketose group. We adopt as a working hypothesis the view that a corresponding structure will be found in other leuco-anthocyanins and that the formation of the anthocyanidins from these precursors is actually the result of oxidation.

The experiments designed to exclude the latter possibility were hardly conclusive; a mere trace of oxygen is required and in any case disproportionation is a possibility that must be reckoned with. No information is available in regard to the quantitative relations of leuco-anthocyanin to pigment produced under different conditions.

If we have correctly interpreted the evidence, the formation of peltogynidin from peltogynol must involve oxidation, but we have not been able to inhibit the appearance of pigment on boiling with hydrochloric acid by taking ordinary measures for the exclusion of oxygen.

In the case of the leuco-anthocyanins a plausible suggestion is that a hydroxyl group of a sugar-chain is involved in the semi-acetal structure with the carbonyl group in position 3 of the pyran nucleus.

EXPERIMENTAL.

Peltogynol.—The first small specimens of woods of *Peltogyne* species were kindly supplied by Miss M. M. Chattaway and Dr. L. Chalk of the Department of Forestry, and the material used in this investigation was a log of the wood of *P. porphyrocardia* obtained from Trinidad through the Department of the Conservator of Forests. It was found that the reddening of the wood on exposure does not occur in the dark even during 4 hours at 40°. In the earlier experiments extraction with 0·5% hydrochloric acid was practised, but the procedure is not advantageous (the wood contains free acetic and butyric acids). Direct fractional extraction with organic solvents gave a large yield of material, but this was very difficult to purify. We are much indebted to Mr. W. Campbell of the Forests Products Research Laboratory, Princes Risborough, for kindly undertaking the comminution of the wood. This proved worth while, as the yields on the weight of wood used were : fine shavings, 1·3%; powdered wood (60—80 or 100 mesh/ sq. in.), 2·3%. The finely divided wood (50 g.) was heated on the steam-bath with water (500 c.c.) for 20 minutes and after filtration the residue was treated in the same way. The combined extracts were saturated with sodium chloride, sodium hydrogen carbonate (10 g.) added, and the cold solution shaken with three successive volumes of ethyl acetate (250 c.c. each). The extracts were kept over anhydrous sodium sulphate (10 g.) and sodium hydrogen carbonate (10 g.) (the latter absorbing a yellow substance, soluble in ether and exhibiting strong co-pigmenting properties in solutions of pelargonidin or cyanidin chlorides) for *ca.* 12 hours, filtered, and concentrated under diminished pressure to about 50 c.c. The solution was filtered through dry sodium sulphate (5 g.) and sodium hydrogen carbonate (5 g.) into light petroleum (300 c.c. of

b. p. 40—60°) with constant stirring. The light mauve solid was triturated with light petroleum (200 c.c. of b. p. 60—70°) and then ground with the convenient minimum of pure ethyl acetate; the isolated solid was then pure enough for many purposes.

Alternatively the solid washed with light petroleum was triturated with water (10 c.c.) for the removal of a soluble yellow impurity, then taken up in ethyl acetate, the solution dried by means of sodium sulphate (2 g.) and sodium hydrogen carbonate (2 g.), and a little benzene added to precipitate a further impurity. The filtered solution was added to light petroleum, and the recovered solid treated twice again in the same manner. It was then almost colourless and was dissolved in warm water and crystallised by concentration of the solution in a desiccator. The colourless, elongated, flat prisms became pink at 200° and darker red at about 240° with gradual softening and decomposition (Found in material dried at 80° in a vacuum : C, 63·7, 63·7, 63·7; H, 4·9, 4·9, 4·9; N, 0·0; MeO, 0·0. $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·6%). $[\alpha]_D^{21°} + 273°$ ($c = 0·6$ in ethyl acetate). The high value for hydrogen is due to the hygroscopic character of the substance.

Another method of purification consisted in washing the crude substance successively with light petroleum (b. p. 60—70°), benzene, chloroform, and a little ethyl acetate. It was then dissolved in ethyl acetate, and the solution concentrated in a vacuum desiccator; the pale bluish crystals were collected, partly dissolved in ethyl acetate (leaving behind most of the coloured impurity), and the solution filtered through a little activated alumina. This removed the whole of the colour, and colourless crystals were obtained on concentration of the solution. If too much alumina is employed, the peltogynol is itself adsorbed and cannot be removed by continuous extraction with acetone or ethyl acetate. As the purification of peltogynol proceeds, it becomes much more sparingly soluble in ethyl acetate, but this is not reflected in changed analytical results and all specimens afforded the same tetra-acetate. Peltogynol is sparingly soluble in cold water, moderately readily in hot water; it is very sparingly soluble in ether, benzene or chloroform, readily soluble in acetone, and freely soluble in the simple alcohols. The plates separating from ethyl acetate become syrupy in contact with water, but the substance quickly crystallises again in a new form. An aqueous or alcoholic solution develops a bright green coloration on the addition of ferric chloride. Pure peltogynol is not discoloured on exposure to light and air.

A full description of peltogynidin and its derivatives will be submitted later, but it may be stated here that the salt obtained by the action of hot hydrochloric acid or cold alcoholic hydrogen chloride on peltogynol is undoubtedly a mixture containing some bimolecular condensation products. The action of bromine on the substance in peroxide-containing dioxan solution (cf. Appel and Robinson, *loc. cit.*) gives a purer product. All specimens of peltogynidin give somewhat bluer-red solutions than cyanidin, but the colour reactions with sodium acetate and sodium carbonate closely resemble those of fisetinidin. The ferric reaction is pure blue in alcoholic solutions and is identical with that displayed by cyanidin. Characteristic of peltogynidin is the bright red coloration produced (through blue) on the addition of sodium hydroxide; no other anthocyanidin exhibits this behaviour.

O-*Tetra-acetylpeltogynol.*—This derivative was prepared on many occasions, substantially as described below, but the reaction was often completed by heating with consequent diminution of the yield. The substance is sparingly soluble in cold methyl and ethyl alcohols, ether, water, and light petroleum ; it is readily soluble in benzene, chloroform, and ethyl acetate and moderately readily soluble in hot ether or alcohol. It crystallises from aqueous acetic acid in colourless, flat, rectangular prismatic needles and best from benzene–alcohol in a similar form or in hair-fine needles on rapid separation, m. p. 173° (Found in material dried at 80° in a vacuum : C, 61·3, 61·3, 61·3; H, 4·8, 4·8, 4·8. $C_{24}H_{22}O_{10}$ requires C, 61·3; H, 4·7%). The determination of acetyl groups invariably gave a high value; for example, Dr. G. Weiler used the method of alkaline hydrolysis, and estimation of the acetic acid isolated by distillation (Found : MeCO, 39·4, 39·3. $C_{24}H_{22}O_{10}$ requires 4MeCO, 36·6%). But peltogynol itself gave MeCO 1·5—2%, and it is evident that a small proportion of a volatile acid is produced by its degradation. Miss Crowfoot's results confirmed the composition attributed to the derivative.

The following is the best method of preparation. A mixture of peltogynol (1 g.), pyridine (1 c.c.), and pure acetic anhydride (12 g.) was made with cooling, kept for 48 hours, and then decomposed with water. The solid was washed with aqueous sodium carbonate and water, triturated with light petroleum, and dried (0·95 g.); after further washing with ether (40 c.c.) and one crystallisation, an almost pure product was obtained (0·64 g. of m. p. 169°) m. p. 173°, after crystallisation from benzene–alcohol ($[\alpha]_D^{20°} + 125°$; $c = 0·4$ in chloroform). Tetra-acetylpeltogynol is not convertible into an acetylpeltogynidin salt, even by means of bromine

and technical dioxan; on heating with alcoholic hydrogen chloride it is gradually hydrolysed and the solution slowly reddens, becoming ultimately intense bluish-red.

The solution of the substance in concentrated sulphuric acid is momentarily colourless, but a pink colour and a bright green fluorescence very quickly make their appearance; the colour deepens to brownish-red and on the addition of water it becomes magenta and the fluorescence disappears. The preparation of a methoxyacetyl derivative of peltogynol was attempted but the product could not be purified.

Peltogynol from Peltogyne pubescens.—A small specimen of the wood was reduced to sawdust, and the peltogynol isolated in the usual way. The substance had the superficial character of the leuco-anthocyanidin previously examined and it was identified by conversion into the tetra-acetyl derivative. This had m. p. 173°, alone or mixed with a specimen from *P. porphyrocardia* (Found : C, 61·3; H, 4·8%). The woods of *Copaifera pubiflora* and *Trachylobium Hornemanianum* contain a leuco-anthocyanidin showing the reactions of peltogynol.

O-Tetrabenzoylpeltogynol.—Benzoyl chloride (6 g.) was added to a cooled solution of peltogynol (2 g.) in the minimum quantity of dry pyridine and after 2 days the mixture was decomposed with water, and benzoyl chloride eliminated by means of sulphanilic acid and aqueous sodium carbonate. The solid product was washed with water, and light petroleum, precipitated from benzene solution by means of light petroleum, washed with cold ether, and crystallised from acetic acid, forming colourless plates, m. p. 244° (Found in material dried at 80° in a vacuum : C, 73·6; H, 4·2. $C_{44}H_{30}O_{10}$ requires C, 73·5; H, 4·2%). The derivative is readily soluble in cold chloroform and moderately readily soluble in ethyl acetate. Direct conversion into peltogynidin salts is very slow, but this may readily be demonstrated after hydrolysis by means of alcoholic potash.

O-Tetra-anisoylpeltogynol.—An anhydrous mixture of peltogynol (1·5 g.), anisoyl chloride (9 g.), and pyridine (6 drops) was kept for 2 days and then decomposed with water. The product was washed with aqueous sodium hydrogen carbonate, water, and light petroleum; it crystallised from acetic acid in colourless plates, m. p. 218° with decomposition to a red solid (Found : C, 68·6; H, 4·5; MeO, 14·5. $C_{48}H_{38}O_{14}$ requires C, 68·7; H, 4·5; 4MeO, 14·8%). The substance is sparingly soluble in methyl alcohol and ether, moderately readily so in acetone, and freely soluble in benzene; it resembles the benzoate in many respects.

O-Tetramethylpeltogynol (III; R, R′ = Me).—Methyl sulphate (25 g.) and the requisite amount of aqueous potassium hydroxide (10%) to maintain alkalinity were alternately added in three portions to a mechanically stirred solution of peltogynol (5 g.) in methyl alcohol (25 g.; acetone was used with identical results) in an atmosphere of nitrogen. After 2 hours, water was added, the product taken up in benzene, and the extract washed with dilute aqueous potassium hydroxide and water. It was concentrated to a small volume and on the addition of light petroleum the crude product (4·5 g.) was precipitated. The derivative was crystallised from aqueous alcohol (50%) and then from methyl or ethyl alcohol, forming colourless, glistening, long, rectangular plates, m. p. 175° (Found : C, 66·8; H, 5·9; MeO, 33·5. $C_{20}H_{22}O_{6}$ requires C, 67·0; H, 6·1; 4MeO, 34·6%). The low value for methoxyl has been observed on several occasions with both the tetramethyl and the trimethyl ether; it is doubtless due to the observed formation of insoluble, partly methylated flavylium iodides. The derivative is moderately readily soluble in most organic solvents ($[\alpha]_D^{20°} + 264°$; $c = 0·73$ in chloroform) and some of its properties have been already mentioned. Especially characteristic is the brilliant green fluorescence of the trimethylpeltogynidin salts obtained by the usual methods (hot hydrochloric acid, cold alcoholic hydrogen chloride or bromine–dioxan); there is little doubt that these salts contain the tetranuclear heterocyclic system of the formula (III).

O-Trimethylpeltogynol (III; R = Me, R′ = H).—(A) The formation of this substance in methylation experiments when the solution was allowed to become acid and then kept for some hours was fortuitous and can easily be avoided as described in the last section. Most of the substance examined was, however, obtained in this way and separated from the tetramethyl ether by taking advantage of its more sparing solubility in organic solvents; it crystallised from ethyl acetate in long flat needles or plates, m. p. 198° (Found : C, 66·2; H, 5·8; MeO, 26·9. $C_{19}H_{20}O_{6}$ requires C, 66·3; H, 5·8; 3MeO, 27·0%). The micro-Zeisel treatment was specially prolonged and lower results were usually obtained (25—26%). The pure substance is sparingly soluble in cold benzene and crystallises from the hot solvent in needles (complete separation from tetramethyl ether); it is readily soluble in cold chloroform ($[\alpha]_D^{20°} + 254°$; $c = 0·236$ in chloroform).

(B) A cold solution of *O*-tetramethylpeltogynol (1 g.) in acetic acid (20 c.c.) and hydrochloric acid (10 c.c. of 15%) was kept under nitrogen for 12 hours; water and benzene were

then added and the product was precipitated from the organic layer by means of light petroleum. The solid was triturated with 50% aqueous acetone, a small quantity of a colourless substance, m. p. above 230°, remaining undissolved; the solution was added to water, and the precipitate washed with methyl alcohol and a little cold benzene and crystallised from benzene and from alcohol. The long, flat, colourless needles had m. p. 198°, alone or mixed with the specimen previously obtained. Direct comparison of the properties also showed that the samples were identical. The significance of this experiment is explained in the introductory section.

The trimethyl ether affords the same trimethylpeltogynidin salt as the tetramethyl ether.

2 : 4-*Dinitrophenylhydrazone of Peltogynol.*—The derivative separated as an orange-red amorphous precipitate when aqueous solutions of peltogynol and of 2 : 4-dinitrophenylhydrazine in 1% hydrochloric acid were mixed and kept for a few hours. On trituration with a little acetic acid a crystalline powder was obtained, but this could not be recrystallised. A warm mixture of peltogynol and dinitrophenylhydrazine in acetic acid was seeded with the powder and, on scratching, the substance crystallised to a small extent on the sides of the vessel; the tube was washed out without removing the adhering crystals and a solution of peltogynol (0·5 g.) and dinitrophenylhydrazine (0·35 g.) in acetic acid (10 c.c.) was filtered into it. The mixture was then heated on the steam-bath for 15 minutes and allowed to cool. Almost the whole of the product separated from the hot solution; it was collected and washed with acetic acid and ether and formed an orange microcrystalline powder consisting of dense aggregates of needles. On heating, darkening commenced at about 190°, the substance was chocolate-brown at 220°, and it exploded at 224° (Found in material dried at 110° in a vacuum over phosphoric oxide : C, 54·5; H, 3·8; N, 11·5. $C_{22}H_{16}O_9N_4$ requires C, 54·8; H, 3·7; N, 11·6%). The substance is very sparingly soluble in most organic solvents, for example, in boiling acetic acid or ethyl acetate, but when impure it dissolves readily in alcohol; it is deposited very slowly indeed when its hot saturated solutions are cooled. The characteristic crimson peltogynidin chloride is obtained on boiling with concentrated hydrochloric acid. The solution in aqueous sodium hydroxide quickly develops an intense violet-brown colour. The ferric reaction in dioxan is an intense yellowish-ivy green coloration.

Oxidation of Peltogynol with Nitric Acid. Formation of Styphnic Acid.—A mixture of peltogynol (1 g.) and nitric acid (10 c.c., d 1·42) was heated over a gauze for 1 minute; dense fumes accompanied the vigorous oxidation. The reaction was allowed to subside and the process twice repeated. After the addition of water (50 c.c.) the solution was extracted with benzene (20 c.c.) and then with toluene (20 c.c.) and the combined extracts were concentrated to 10 c.c. The crude styphnic acid was precipitated by the addition of light petroleum and crystallised twice from ethyl acetate and again from benzene–toluene, forming almost colourless, flat needles and rectangular plates, m. p. 175°, alone or mixed with an authentic specimen. The substance tallied with styphnic acid in its properties and for further confirmation the highly characteristic compound with naphthalene and acetone was prepared. This crystallised from acetone in long yellow needles, which were washed with ether and then had m. p. 163—164°, alone or mixed with an authentic specimen. With the aid of this derivative more styphnic acid could be obtained from the aqueous solution already extracted with benzene and toluene by further extraction with ethyl acetate. This procedure gave a product too impure for direct crystallisation.

Attempts to demonstrate the resorcinol nucleus by potash fusion of peltogynol were only partly successful; the products gave the fluorescein reaction.

Oxidation of Trimethylpeltogynol with Nitric Acid.—O-Trimethylpeltogynol (2·2 g.) was heated on the steam-bath with nitric acid (50 c.c., d 1·42) and water (25 c.c.) until the vigorous evolution of fumes ceased; the liquid was then concentrated to one half its bulk and refluxed for 15 minutes. Finally most of the nitric acid was removed by distillation, and the residue mixed with water and extracted with ether. The ethereal layer was washed with aqueous sodium carbonate (probably removing styphuric acid) until the washings were colourless, then dried, and evaporated; the residue crystallised and was thrice recrystallised from ethyl alcohol, eventually forming pale yellow needles, m. p. 131° alone or mixed with authentic 4 : 5-dinitroveratrole. 2 : 3-Dimethoxyphenanthraphenazine was also prepared from the dinitroveratrole obtained as above and this derivative exhibited the characteristic violet fluorescence in benzene solution and magenta coloration in sulphuric acid solution.

Oxidation of Trimethylpeltogynol with Potassium Permanganate.—Although dioxan is not really adequately stable to permanganate, the oxidation was conducted in this solvent. A solution of potassium permanganate (10 g.) in water (300 c.c.) was gradually added to one of O-trimethylpeltogynol (3·5 g.) in pure dioxan (75 c.c.), mixed with saturated aqueous sodium

carbonate (10 c.c.), and heated on the steam-bath. The oxidation was slow at first, and when the permanganate was reduced, the straw-yellow filtered solution was concentrated to 100 c.c. and acidified with hydrochloric acid. The precipitated ochreous acid (filtrate A) was washed with ether and dried (0·56 g.). The substance was dissolved in acetone, the solution decolorised with the minimum of activated alumina and added to a large volume of pure ether, and the filtered ethereal solution thoroughly washed with water. It was then dried over sodium sulphate and concentrated to a small volume. The acid separated as a colourless microcrystalline crust and it was further purified by a repetition of the process (Found in material dried at 110° in a high vacuum over phosphoric oxide : C, 63·5; H, 5·3; MeO, 25·2. $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0; 3MeO, 26·0%. $C_{19}H_{20}O_7$ requires C, 63·3; H, 5·5%). The substance, which gradually decomposes and chars above 200° without melting, is readily soluble in alcohol and acetone, sparingly so in benzene and ether; it yields a red flavylium salt on treatment with bromine in hot technical dioxan solution. The formula $C_{19}H_{18}O_7$ is the more probable and we consider that this O-*trimethylpeltogynic acid* is to be represented by the expression
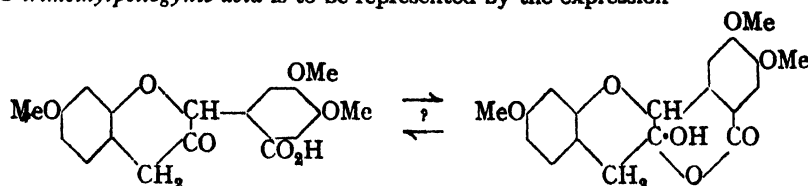
The Congo-red reaction of the filtrate (A) was removed by the addition of sodium acetate, and calcium oxalate then precipitated by means of calcium chloride; the clear centrifuged liquid was saturated with sodium chloride, strongly acidified with hydrochloric acid, and repeatedly extracted with ether. The ethereal solution was dried and evaporated, leaving a considerable crystalline residue of *m*-hemipinic acid. This was recognised by the formation of the characteristic silver hydrogen *m*-hemipinate and by that of the anhydride, which sublimed in leaflets, m. p. 175°. The acid was dissolved in an excess of aqueous ethylamine, and the solution distilled, finally by strong heating in a glass tube. The ethylimide obtained as a distillate and sublimate crystallised from alcohol in almost colourless needles, m. p. 230° alone or mixed with an authentic specimen (Found : C, 61·2; H, 5·6; N, 5·9. Calc. for $C_{12}H_{13}O_4N$: C, 61·3; H, 5·5; N, 5·9%).

The manganese precipitate was suspended in water, and the manganese dioxide dissolved by passing sulphur dioxide. The pale pink flocculent residual precipitate consisted of unchanged trimethylpeltogynol mixed with a large proportion of a much more sparingly soluble substance; it was not further examined, as similar material has been obtained in other ways and it is surmised that condensation of two molecules is responsible for such deterioration.

O-*Tetramethylfisetinidin Chloride.*—This salt was obtained in quantitative yield by the passage of hydrogen chloride into a cold solution of *p*-methoxysalicylaldehyde (0·5 g.) and ω : 3 : 4-trimethoxyacetophenone (0·7 g.) in ethyl acetate (10 c.c.). It crystallised, in deep brown needles with a green glance, almost completely from the reaction mixture; it crystallised well from 6% hydrochloric acid in chocolate needles (Found in air-dried material : C, 53·3, 53·4; H, 6·1, 6·2; MeO, 28·7. $C_{19}H_{19}O_5Cl,3·5H_2O$ requires C, 53·6; H, 6·1; 4MeO, 29·2%). The salt exhibits the usual properties of its type; it gives readily a colourless pseudo-base and its solutions have the usual bluish-red (alcoholic) to orange-red (aqueous) colour, less blue-toned than cyanidin derivatives and much less blue-toned than peltogynidin salts under similar conditions. The aqueous and alcoholic solutions are non-fluorescent. If a solution of formaldehyde, trioxymethylene or methylene sulphate in sulphuric acid is added to a cold solution of the salt in the same solvent, a rapid change towards a bluish-red tone is observed; at the same time, intense green fluorescence is developed and on dilution a fluorescent solution is obtained which tallies closely with one of trimethylpeltogynidin salts. The further stages of this investigation will be reported subsequently, but the significance of even the qualitative observation cannot be overlooked.

The following report has been submitted by Miss D. Crowfoot, to whom we are greatly indebted.

Peltogynol.—Monoclinic needles elongated along *b*, flattened on (001). Birefringence positive and very high. Large optic axial angle.

X-*Ray data.* $a = 7·91$ (limits 7·89, 7·99), $b = 7·32$ (limits 7·30, 7·35), $c = 23·25$; $\beta = 72°$. $c \sin \beta = 22·34$ (limits 22·22, 22·46), $a \sin \beta = 7·52$. $P = 1·535$ (limits 1·531, 1·538). $M = 301$ *

* $C_{16}H_{14}O_6$ requires M, 302; $C_{24}H_{22}O_{10}$ requires M, 470.

(limits 296, 297) with $n = 4$. Space group *P*2, from (0*k*0) halved when *k* odd. There are therefore two molecules in the asymmetric unit. There is also a halving of (00*l*) with *l* odd not required by symmetry, which suggests that these two molecules are related approximately by a screw axis along ⊥ (001). The dimensions of the unit cell and the kind of optics suggest lath-shaped molecules (*i.e.*, that one dimension is decidedly longer than the other two), arranged flat in *b*—the α optic direction.

The requirements fit very closely with formula (I) (p. 746), from which a plausible structure can be devised. Formula (II) is very difficult to fit at all. Its great breadth can just be fitted by allowing considerable slanting in *b*, but even so the length is shorter than would be expected.

Acetyl Derivative of Pellogynol.—Long needles. Orthorhombic elongated along *b* with *m* faces developed. {101}. Birefringence high, positive. Small optic axial angle. *a* = β, *b* = α, *c* = γ.

X-Ray data. $a = 13.26$, $b = 5.70$, $c = 30.10$. (*h*00), (0*k*0), (00*l*) halved for *h*, *k*, *l* odd respectively. Space group *P*2, 2, 2. $n = 4$. $M = 473 \pm 6.$*

The dimensions found and the optics associated with them immediately suggest a parallel with certain types of crystallographic arrangement found in the sterols. Such an analogy would be reasonable if the structure of this compound were based on (I), not on (II).

The breadth of (II) again is difficult to fit into the αβ section as would be required if the straightforward interpretation is given to the optics. This is not required, however, by ortho-rhombic symmetry as it is by monoclinic. But any structure based on (II) seems to be much less satisfactory than those derived from (I).

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168. *The Constitution of Cyanomaclurin.*

By HERBERT APPEL and ROBERT ROBINSON.

CYANOMACLURIN, isolated by A. G. Perkin and Cope (J., 1895, **67**, 939) from jackwood (*Artocarpus integrifolia*), was later more fully examined by Perkin (J., 1905, **87**, 715), who suggested the structure (I) (discussing also two other formulæ which may now be definitely ruled out) largely on the grounds of the general resemblance exhibited to catechin and the degradation of the substance, on fusion with potash, to phloroglucinol, β-resorcylic acid, and resorcinol. This view of the constitution of the substance was supported by the preparation of supposed penta-acetyl and pentabenzoyl derivatives, but it must be stated at once that we now regard these as tetra-acylcyanomaclurins.

Perkin's penta-acyl derivatives being assumed to be correctly so described, the optical activity of cyanomaclurin recorded in this communication would require the slight modification to (II).
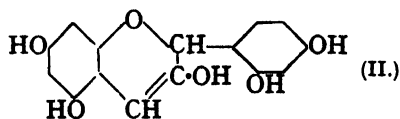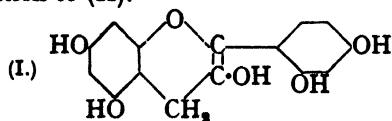
Through the kindness of Professor A. G. Perkin, a small quantity of cyanomaclurin was available for investigation, and we first sought evidence of the fundamental correctness of (I) and (II) in respect of the carbon–oxygen skeleton. This could best be obtained by oxidation of cyanomaclurin to morin or to a morinidin salt and in the latter connection our experiments on the conversion of catechin into cyanidin chloride were instituted (this vol., p. 426). The action of bromine on cyanomaclurin in dioxan solution afforded pink solutions, but the morinidin bromide could not be isolated in this way.

The very striking deep blue colour developed on gentle heating of alkaline solutions of cyanomaclurin (hence the name) was, however, very like that of a solution of morinidin in dilute aqueous sodium hydroxide, and similar changes occurred on heating, keeping, or acidifying the solutions.

It seemed possible that cyanomaclurin is actually converted into the salt of morinidin-colour-base by the action of warm alkalis, possibly as the result of autoxidation (aeration)

* $C_{16}H_{14}O_6$ requires M, 302; $C_{24}H_{22}O_{10}$ requires M, 470.

or of a disproportionation of Cannizzaro-reaction type. Under special conditions we were able to show that the cyanomaclurin alkali-reaction is actually to be explained in this way, although we isolated only a few mg. of pure morinidin chloride after acidification of the solution. This was due in part to the very small amount of cyanomaclurin remaining at this stage and in part to difficulties in the purification similar to those encountered in the synthesis of morinidin chloride (Charlesworth, Chavan, and Robinson, J., 1933, 370). Direct comparison with an authentic specimen established the identity of the morinidin salt to our satisfaction.

The skeleton having been recognised, we were in a better position to consider the actual detail of the alternative formulæ, which must embrace a ketone (III) and a semi-acetal (IV) in addition to (II).

(III.) ...structure... (IV.)
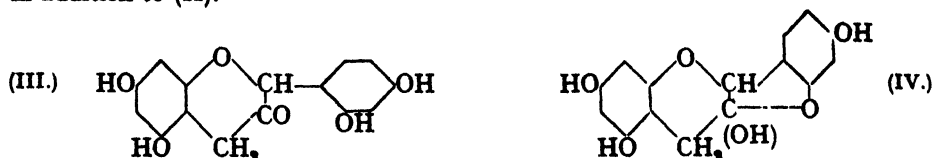
A re-examination of the acetyl derivative of cyanomaclurin showed that it is a tetra-acetyl compound (OAc estimations) and the same observation was made in regard to the tetra-benzoylcyanomaclurin (C and H estimation). Actually the theoretical values (C, H) for the tetra- and the penta-acetate are not very different. The choice seems then to lie between (III) and (IV), and we preferred the latter because it explained the failure of cyano-maclurin to be oxidised readily in acid solution with formation of morinidin salts. We considered that in neutral or acid solutions cyanomaclurin is (IV) and that in alkaline solution the ring might be broken with formation of (III), which then suffered oxidation to morinidin-colour-base. We were naturally well aware that the semi-acetal group is not *directly* hydrolysed by alkalis and the view we took was that the ring fission was a process consequent on salt-formation through the phenolic hydroxyls. In other words it might be the result of a change in stability due to the assumption of the anionic charge. The fact that cyanomaclurin does not exhibit mutarotation cannot be cited against (IV) so long as the possibility remains open that the modification (III), or its hydrate, represents an unfavoured configuration. Mutarotation would hardly be due to ring closure in *cis-cis* and *cis-trans* forms; one of these would doubtless preponderate or even be produced exclusively in the open-chain semi-acetal equilibria.

The formula (IV) is also favoured by the correspondence between catechin and cyano-maclurin in many reactions, including so-called phlobaphene formation. The natural flavanones are in general quite stable to hot dilute acids and, although the contrast with cyanomaclurin might be attributed, on the basis of (III), to the removal of the carbonyl group from direct attachment to the phloroglucinol nucleus, yet (IV) offers an even more natural explanation. The conclusive argument in favour of (IV) is derived from the preparation of an amorphous *trimethyl* ether of cyanomaclurin. This is insoluble in aqueous alkalis (a proof that, as suggested above, the semi-acetal group is not itself directly affected by alkalis) and it does not yield a semicarbazone. It forms a *monoacetyl* derivative, also amorphous. The poverty of our resources precluded a further examination of these derivatives.

EXPERIMENTAL.

Optical Activity of Cyanomaclurin.—In ethyl acetate (c, 1·0), $[\alpha]_D^{20°} + 215°$; in water (c, 0·94), $[\alpha]_D^{20°} + 192°$. No mutarotation was observed in either case; a drop of aqueous ammonia was added to the aqueous solution (0·5 c.c.) and the rotation was unchanged during 10 minutes; further observation was hindered by the development of a red coloration. As the asymmetric carbon atom is contiguous to a carbonyl group, or potential carbonyl group, it might be thought surprising that cyanomaclurin retains its optical activity during the process of isolation. Dr. A. Weissberger contributes, in this connection, a note which shows that even *d*-benzoin is racemised with difficulty in acid solution:

" *d*-Benzoin dissolved in *ca.* 0·3N-alcoholic (90%) hydrogen chloride showed no observable

change of rotatory power after keeping at room temperature for 18 hours. On boiling, the rotatory power was diminished by 20 per cent. of its value in the course of 1 hour."

Tetra-acetylcyanomaclurin.—Professor Perkin's specimen was examined (Found: MeCO, 38·2. $C_{20}H_{20}O_{10}$ requires C, 60·5; H, 4·4; 4MeCO, 37·7%. $C_{25}H_{26}O_{11}$, penta-acetate, requires C, 60·2; H, 4·5; 5MeCO, 43·2%). In ethyl acetate (c, 1·2), $[\alpha]_D^{20°}$ was found to be $+ 95°$.

Tetrabenzoylcyanomaclurin.—Professor Perkin's sample (Found: C, 72·7; H, 4·1. $C_{43}H_{30}O_{10}$ requires C, 73·3; H, 4·0%. $C_{50}H_{34}O_{11}$, pentabenzoate, requires C, 74·2; H, 4·0%). The presence of a small proportion of the tribenzoyl derivative is indicated.

O-*Trimethylcyanomaclurin.*—Aqueous potassium hydroxide (2 c.c. of 50%) was added drop-wise to a mixture of cyanomaclurin (0·2 g.), methyl sulphate (2 c.c.), and methyl alcohol (5 c.c.) cooled in running water. When the methyl sulphate was decomposed, water was added and the product (0·2 g.) was collected and purified by careful addition of water to its alcoholic solution. The colourless substance was amorphous or indefinitely crystalline, m. p. 73—85° (Found: MeO, 28·5. $C_{18}H_{18}O_6$ requires 3MeO, 28·2%). The derivative is certainly not a phenol, for it is insoluble in dilute aqueous sodium hydroxide and it exhibits no ferric reaction in alcoholic solution. It was recovered unchanged after heating for 75 minutes with an excess of semi-carbazide acetate in alcoholic solution. Rather surprisingly there was no evidence of the form-ation of a morinidin derivative on heating with bromine in hot peroxide-containing dioxan.

The trimethyl ether (30 mg.) was heated with acetic anhydride (1 c.c.) and a drop of pyridine for 5 minutes at 100°. After keeping for 48 hours at the room temperature, the acetyl derivative was isolated, dissolved in a little alcohol, an equal volume of water added, and the mixture concentrated in a desiccator. The white amorphous solid that separated was washed with water and collected. It was similar to the initial material but more readily soluble in aqueous alcohol (Found: MeCO, 10·1. $C_{20}H_{20}O_7$ requires MeCO, 11·6%).

Morinidin Chloride from Cyanomaclurin.—Cyanomaclurin (0·15 g.), dissolved in water (30 c.c.), was added to a solution of sodium carbonate (12·5 g.) in water (500 c.c.) previously heated to 95°. The mixture was shaken and immediately poured on crushed ice. The deep blue solution exhibited the characteristic dichroism (blue and red) of alkaline morinidin solutions; it was acidified with hydrochloric acid, and the oxonium salt extracted by *iso*amyl alcohol (120 c.c.). The extract was shaken with 7% hydrochloric acid, separated, filtered, and mixed with 7% hydrochloric acid (30 c.c.) and light petroleum (1000 c.c.). The morinidin chloride that separated was collected and dissolved in a little alcohol and after the addition of 7% hydro-chloric acid (6 c.c.) the solution was concentrated under diminished pressure. A few mg. of pure morinidin chloride were obtained; the greater part of the salt remained in the aqueous hydrochloric acid solution and could not be isolated therefrom in a pure condition. The ex-periment was twice repeated with the same results. The morinidin chloride so obtained was compared with a specimen prepared according to the method (B) (Charlesworth, Chavan, and Robinson, *loc. cit.*, p. 373) and the two products behaved in identical fashion in so far as the colour reactions and other properties already described were concerned; the material made from cyanomaclurin was, however, more densely aggregated and dissolved the more slowly in hot dilute hydrochloric acid on that account. Continued boiling of a solution in $N/10$-hydrochloric acid caused decolorisation and the colour was not restored on the addition of hydrochloric acid; the two specimens showed the same behaviour in this respect. In order to obtain solutions for comparison of the distribution ratios the following procedure was adopted in order to avoid inequalities in the formation of the colourless transformation product. The synthetic specimen (10·01 mg.) was dissolved in ethyl alcohol (25 c.c.) with the gradual addition of N-hydrochloric acid (25 c.c.) and water (225 c.c.). The specimen from cyanomaclurin (4·23 mg.) was made up to a solution in approximately $N/10$-hydrochloric acid in the same way, the proportionate volume of alcohol being used. The solution from the cyanomaclurin specimen was a little the weaker and the comparison solution was therefore diluted with a mixture of alcohol and nine times its volume of $N/10$-hydrochloric acid until the concentrations were identical; only a few c.c. were required. The properties of these solutions were identical in every respect. They were orange-red, and salmon-red in thin layers; the alkali-colour reactions were again observed and tallied with previous descriptions. Comparisons of the coloured zones made by floating the solutions on saturated sodium acetate and saturated sodium carbonate solutions were made. The be-haviour on addition of zinc dust was also noted. Morinidin chloride shows characteristic distribution between dilute hydrochloric acid and mixtures of toluene and *cyclo*hexanol; in comparison with cyanidin chloride, less of the *cyclo*hexanol needs to be added in order to produce solubility in the mixed organic solvent. The two solutions behaved again in the same way and the organic layers made as described were colorimetrically identical. Equal volumes of the

prepared morindin solutions and the *cyclo*hexanol–toluene mixtures were shaken together. *cyclo*Hexanol (1 vol.) and toluene (3 vols.) (CT3) dissolved the whole of the pigment to a reddish-violet solution. CT6 gave a distribution, a slightly bluer-violet organic layer and a pale salmon aqueous layer. The graded series CT7—CT12 was examined, the organic layer in the last case being pale violet.

The following report of an examination of *O*-tetra-acetylcyanomaclurin is submitted by Miss D. Crowfoot.

The crystals are monoclinic needles, elongated along *b* and slightly flattened on (100). Birefringence negative. Plane of the optic axes (010). γ slightly inclined to (100).

X-*Ray data* : $a = 15 \cdot 1 \, \alpha$, $b = 6 \cdot 5 \, \beta$, $c = 23 \cdot 7 \, \gamma$; $\beta = 74°$. $0k0$ halved when *k* is odd. Space group $P2_1$. Number of molecules in unit cell = 4, if $\rho = 1 \cdot 27$, *i.e.*, number in asymmetric unit = 2.

The fact that there are two molecules in the asymmetric unit makes it difficult to limit the crystallographic possibilities of the arrangement of the molecules sufficiently to distinguish with any certainty the chemical differences. There is, however, a general weakening of the intensities of the planes ($h0l$) when *l* is odd, which suggests that these two molecules are crystallographically related by an approximate *c* glide plane of symmetry. On the basis of these results it is difficult to make a decision between the ketonic and the cyclic ketose acetate formula, both of which can accommodate the data.

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169. *Experiments on the Synthesis of Physostigmine (Eserine). Part XI. The Later Phases of the Synthetical Investigations.*

By FREDERICK E. KING and ROBERT ROBINSON.

THE chief steps in the progress of the attack on physostigmine from the synthetical angle are the following :

(1) The synthesis by Stedman (J., 1924, **125**, 1373) of physostigmol ethyl ether (I, R = Et), and of the methyl ether (I, R = Me) by Späth (*Ber.*, 1925, **58**, 518), which established the presence of the indole nucleus and the orientation of certain substituents.

(2) The synthesis *and resolution* of dehydroesermetholemethine metho-salts (II) (King and Robinson, Part V, J., 1932, 326). The identity of the synthetic salts with those derived by degradation of the alkaloid established for the first time the existence of the angle methyl group and gave important support to the view of the constitution of eserine which is now generally accepted. As this fact does not seem to have been recognised by other workers in the field, we venture to draw attention to it.
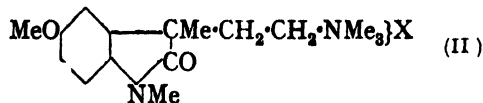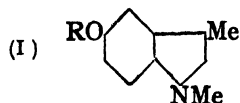
(3) Various syntheses of the eserine ring system, for example, that of *dl-nor*eserethole (III), first accomplished by Robinson and Suginome (J., 1932, 304), and *dl-nor*esermethole (King and Robinson, *ibid.*, p. 1433) ; and also improvements in the methods, due to King, Liguori, and Robinson (J., 1933, 1475), Hoshino and Tamura (*Proc. Imp. Acad. Japan*, 1932, **8**, 171 ; *Annalen*, 1933, **500**, 42), Hoshino and Kobayashi (*Proc. Imp. Acad. Japan*, 1934, **10**, 99, 564 ; *Annalen*, 1935, **516**, 81), Hoshino and Kotake (*ibid.*, p. 76), Julian, Pikl, and Boggess (*J. Amer. Chem. Soc.*, 1934, **56**, 1797), and Julian and Pikl (*ibid.*, 1935, **57**, 539, 563).

(4) The resolution of *dl-nor*eserethole and its conversion into optically active eserethole metho-salts identical with those derived from eserine by successive hydrolysis, ethylation, and *N*-methylation (Hoshino and Kobayashi, *loc. cit.*).

(5) The final stage, chronologically the first to be accomplished, namely, the conversion of eseroline into eserine (Polonovski and Nitzberg, *Bull. Soc. chim.*, 1916, **19**, 33).

This is the position at the time of writing,[*] and the total synthesis of eserine may eventually be realised by way of several routes, of which the following is one of the more promising :

dl-noreserethole ⟶ l-noreserethole ⟶ l-eseretholemetho-salt ⟶ l-eserethole ⟶ l-eseroline ⟶ eserine.
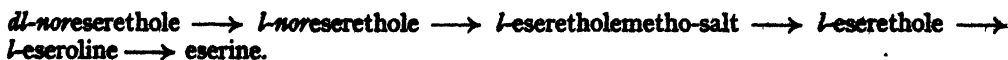
The necessary stage, eserethole ⟶ eseroline, has not been effected hitherto and, although the yields are not yet satisfactory, we have bridged this particular gap by experiments described in the present communication.

Unfortunately the eserethole metho-salts cannot be thermally decomposed without breaking of the ring system. Reference to this difficulty was made when the degradation of l-esermethole methochloride was described (J., 1933, 270), and we now find that the related eserethole salt behaves in a similar manner, affording only physostigmol ethyl ether. The methofluoride, on the other hand, distils partly unchanged (!) (at least the distillate gives the methopicrate on treatment with picric acid), and is partly decomposed with the formation of a base not yet identified, but which from the nature of its picrate is certainly not l-eserethole.

Eserethole metho-salts are much more smoothly de-ethylated by means of hydrobromic acid than eserethole itself, and in this way hitherto unknown eseroline metho-salts have been obtained which were identified in the form of *eseroline methopicrate*.

The completion of the synthesis of eserine along the lines of the present series of memoirs, therefore, requires yet a further stage, which might be one of the following : (a) the resolution of dl-eserethole, (b) the N-demethylation of an eserethole metho-salt, or (c) the N-demethylation of an eseroline metho-salt.

(III)   EtO —⟨ ⟩— ĊMe—ĊH₂ / ĊH\ /CH₂ / NMe   NH

(IV)   EtO —⟨ ⟩— ĊMe—ĊH₂ / ĊH\ /CH₂ / NMe   NMe

The important intermediate dl-noreserethole (III) is a rallying point, because the description of its derivatives shows that the same substance has been obtained both in the course of this series of investigations and by the Japanese and American chemists. On controlled methylation with methyl p-toluenesulphonate we found that it yielded a crystalline dl-eserethole (IV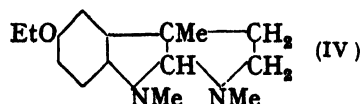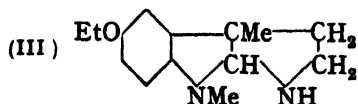), m. p. 79—80° (J., 1934, 1416), and we then surmised that this substance would prove to be identical with a base, m. p. 80—81°, obtained by Hoshino and Kobayashi (*Proc. Imp. Acad. Japan*, 1934, 10, 99). Through the kindness of these authors we have been able to confirm this view by a direct comparison of the specimens. Hoshino and Kobayashi, however, described their base as having the composition $C_{16}H_{24}ON_2$ and have recently reaffirmed this view (*ibid.*, p. 564). We can only reply that three separate sets of estimations (that originally published, which was by Schoeller, and five more by Weiler and by Roth) of carbon and hydrogen support our view that the base is $C_{15}H_{22}ON_2$, and we can also confirm the statement already made (*loc. cit.*, 1934, 1416) that there are only two methyl groups attached to nitrogen. In our opinion the base is structurally identical with eserethole, and it may be a stereoisomeride of this base. We accept the evidence of Hoshino and Kobayashi (*loc. cit.*) that the substance is not dl-eserethole, although the facts leading to this conclusion have not fallen within our experience. It is relevant to note that Linstead and Meade (J., 1934, 935) have isolated cis-cis- and cis-trans-isomerides of fused dicyclooctanes (two five-membered rings), and we provisionally regard the isomerism of dl-eserethole-a, m. p. 38° (synthesised by Julian and Pikl, loc. cit.), and our dl-eserethole-b, m. p. 80°, as another case of the same kind. The fact that the behaviour of dl-eserethole-a and dl-eserethole-b towards methyl iodide is different is not surprising, because the stereochemical hypothesis closely concerns the configuration of the nitrogen atoms.

* The completion of the synthesis of eserine has meanwhile been announced by Julian and Pikl (*J. Amer. Chem. Soc.*, 1935, 57, 755), but, as this paper arrived in England after the present MS. had been submitted to the Society, we must reserve our comment.

The formula (V) formerly attributed by Hoshino and Kobayashi to their base of the supposed formula $C_{16}H_{24}ON_2$ has not been abandoned by these authors, but they do not print it in their recent publication in the *Annalen*.

A similar, highly improbable constitution is attributed by Julian and Pikl to a monopicrate (VII) made from eserethole dimethodipicrate (VI) by loss of picric acid on crystallisation from alcohol.

| (V.) | (VI.) | (VII.) |

EtO—⟨ ⟩—CMe—CH₂ / CH₂ NMe₂ NMe   (V.)

EtO—⟨ ⟩—CMe—CH₂ / CH · CH₂ NMe₂ NMe · O·C₆H₂(NO₂)₃ O·C₆H₂(NO₂)₃   (VI.)

EtO—⟨ ⟩—CMe—CH₂ / CH₂ NMe₂ NMe₂ · O·C₆H₂(NO₂)₃   (VII.)
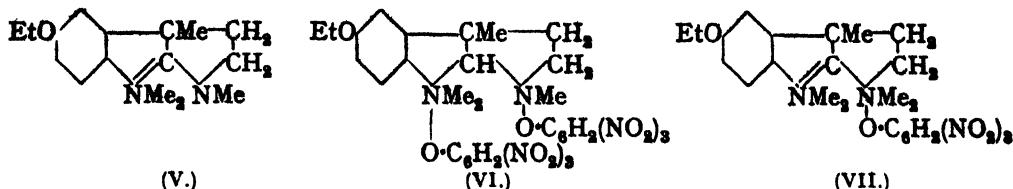
Julian and Pikl also support the formula (V) as an expression for our base, m. p. 80°, but without any new evidence other than the synthesis of an isomeride. As they imply violations of fundamental theory, the expressions (V) and (VII) cannot be accepted, and furthermore, a dipicrate that loses picric acid on recrystallisation can hardly be a diquaternary picrate. It is probably a tertiary-quaternary picrate with a methyl group less than Julian and Pikl suppose.

EXPERIMENTAL.

Comparison of Specimens by Melting Point Determinations.—The following observations are made concerning the three specimens supplied by Hoshino and Kobayashi :

(1) The *dl*-noreserethole picrate of m. p. 180—181° was indistinguishable from the material of Robinson and Suginome (J., 1932, 314), who recorded m. p. 180—181°, not 191—192° as recently quoted in error (J., 1934, 1416).

(2) *dl*-Eserethole-*b*, for which the Japanese chemists claim m. p. 80—81°, when mixed with our substance of m. p. 79—80°, melted at 77—79°. It was then found that their specimen actually had m. p. 77°.

(3) *dl*-Eserethole-*b* picrate. For this substance the m. p.'s 138—140° (King, Robinson, and Suginome, J., 1933, 1474), 139—140° (King, Liguori, and Robinson, J., 1934, 1418), and 140—141° (Hoshino and Kobayashi, *Proc. Imp. Acad. Japan*, 1934, 10, 99) have been recorded. The m. p. has since been stated as 150—151° (Hoshino and Kobayashi, *Annalen*, 1935, 516, 87), which we have verified for the sample received. On admixture with either of the two specimens, m. p. 138—140° and 139—140°, no depression was observable, and it was then discovered that both of these now have m. p. 150—151° ! It is therefore supposed that the picrate of the base m. p. 80° is dimorphic, the two modifications having m. p. *ca.* 140° and 150—151° respectively.

Analyses of dl-*Eserethole*-b, *m. p.* 80°.—As this matter has to some extent become one in which the reliability of analytical technique is involved, we append the actual figures in order that those who carried out the determinations may be able to identify the experiments (weights in mg.).

R.W. 347.	Substance.	CO_2.	%C.	H_2O.	%H.
	3·562	9·590	73·43	2·810	8·83
	3·657	9·870	73·61	2·935	8·95
	3·820	10·250	73·18	3·040	8·90

These analyses were carried out with different apparatus by three different analysts. The blank tests showed an error of C, − 0·04, 0·01; H, 0·16, − 0·07. G. Weiler.

R.R. 49.	Substance.	CO_2.	%C.	H_2O.	%H.
	4·329	11·59	73·02	3·52	9·10
	3·673	9·84	73·07	2·95	8·99
		p.	*t*°.	*v* (c.c.).	%N
	4·167	746	21	0·408	11·16
	3·867	746	20	0·371	10·97
		AgI.			%C_2H_5O.
	4·536	4·440			18·77
	4·166	4·085			18·81
		AgI (total).	AgI (less OEt).		%NMe.
	4·169	10·740	6·656		19·70
	4·778	12·335	7·654		19·77 H. Roth.

Calc. for $C_{15}H_{22}ON_2$: C, 73·2; H, 8·9; N, 11·4; OEt, 18·2; 2NMe, 23·4%.
Calc. for $C_{16}H_{24}ON_2$: C, 73·8; H, 9·2; N, 10·8; OEt, 17·5; 2NMe, 22·7%.

De-ethylation of 1-*Eserethole and of* 1-*Eserethole Methiodide.*—(i) *Experiments with hydriodic acid.* A solution of *l*-eserethole (0·9 g.) in colourless redistilled hydriodic acid (12 c.c., *d* 1·7) was heated in a stream of pure carbon dioxide by an oil-bath at 140—150°. Evolution of ethyl iodide appeared to be complete within 15 minutes, but much iodine had been liberated, and dilution with water precipitated a tarry material. After being cleared with ether, the acid solution was neutralised with sodium bicarbonate and immediately extracted both with ether and with chloroform, but no pure substance could be isolated.

When *l*-eserethole methiodide (0·7 g.), m. p. 171°, dissolved in the pure acid (10 c.c.), was heated under the above conditions for 12 minutes, the amount of iodine liberated was considerably diminished. On evaporation to dryness at 50° under reduced pressure, the residue was a dark red gum, which was washed with ethyl acetate, dissolved in alcohol, and treated with alcoholic picric acid. The charcoaled solution when quite cold was decanted from a resinous deposit, and the yellow woolly aggregates of needles (0·2 g., softening *ca.* 160° and decomposing at 190°) which had separated after 48 hours were collected and thrice crystallised from alcohol. Stout irregular orange-yellow prisms, m. p. 193—195° (decomp.), were thus obtained, later identified as 1-*eseroline methopicrate* (Found : C, 52·3; H, 5·1; N, 14·9. $C_{20}H_{23}O_8N_5$ requires C, 52·1; H, 5·0; N, 15·2%).

(ii) *Experiments with hydrobromic acid.* A solution of *l*-eserethole (0·9 g.) in colourless redistilled hydrobromic acid (12 c.c., *d* 1·5) was heated, as already described, in a carbon dioxide atmosphere at 145—150° for 50 minutes, and then evaporated at 50° under diminished pressure. The pale olive-green residue was dissolved in hot alcohol (18 c.c.) containing picric acid (1 g.), and after 24 hours the precipitated salt was collected and once recrystallised. The product (0·45 g.) then decomposed above 160—170°, but after further recrystallisation compact rosettes of deep yellow prisms were obtained, m. p. 195° (decomp.) after slight sintering at 160—165° (Found : C, 50·8; H, 4·7; N, 15·5. Calc. for *l*-eseroline picrate, $C_{19}H_{21}O_8N_5$: C, 51·0; H, 4·7; N, 15·7%).

The experiment was then repeated with the methiodide (1 g.), and the pale green gum remaining after evaporation of the hydrobromic acid was dissolved in hot alcoholic picric acid (0·65 g. in 22 c.c.). By decanting the cold solution from a small quantity of resin, then boiling with charcoal and filtering, a voluminous mass of yellow needles was obtained, softening at 160—170° and decomposing above 190°. The yield of *l*-eseroline methopicrate reached 0·7 g. or 59%, but was considerably reduced by recrystallisation, since relatively large volumes of alcohol (20—25 c.c.) were required to render the specimen of analytical purity (orange-yellow prisms, m. p. 194—195°, decomp.) (Found : C, 52·0; H, 5·1; N, 15·0%).

1-*Eseroline Picrate and* 1-*Eseroline Methopicrate.*—The eseroline salts required for the identification of the foregoing products were obtained from a sample of the base prepared by the method of Polonovski (*Bull. Soc. chim.*, 1915, 17, 239). The product, which was more conveniently extracted with chloroform, when washed with a little ether and once crystallised from chloroform–light petroleum, had m. p. 125—127° (literature, 128°, 129°) : yield, 78%.

The picrate, which was obtained by mixing equivalent amounts of base and acid in alcoholic solution, after several crystallisations from alcohol, separated in clusters of orange-yellow prismatic crystals, m. p. 195° (decomp.), with softening at 160—165° (Found : C, 50·9; H, 4·9; N, 15·4. Calc. for $C_{19}H_{21}O_8N_5$: C, 51·0; H, 4·7; N, 15·7%). This is in agreement with Salway's description (J., 1912, 101, 982), who gives m. p. 195°, but it remains to be ascertained whether softening at 160—165° is characteristic of the salt derived from highly purified eseroline. It is perhaps significant that the specimen of this picrate having its origin in eserethole (*vide supra*) also has this feature. Other authorities give m. p. 190° (Polonovski, *loc. cit.*) and 167° (Strauss, *Annalen*, 1913, 401, 350), but the latter is thought to refer to a dimorphic form.

The addition of an equivalent of methyl iodide to an acetone solution of eseroline (m. p. 125—127°) precipitated the methiodide in colourless hexagonal plates, m. p. 192—194° (literature, 196°). An alcoholic solution of the requisite quantity of picric acid gave a mass of yellow needles, which on recrystallisation yielded the methopicrate, m. p. 194—195° (decomp.), identical in form and analysis with the specimens described above (Found : C, 52·0; H, 5·0; N, 15·1%).

Thermal Decomposition of 1-*Eserethole Quaternary Salts.*—(i) *Eserethole methochloride.* A solution of the methiodide (2·5 g.) in alcohol (6 c.c.) and water (25 c.c.) was digested for a few minutes at 100° with freshly prepared silver chloride (7·5 g.). After filtration, the solution was

evaporated at 55° (reduced pressure), and the solid product dissolved in acetone (*ca.* 15 c.c.). When diluted with an equal volume of ethyl acetate, the solution yielded colourless stout prisms (1·7 g.), softening at 126—127°, m. p. *ca.* 175°.

When the salt was heated in a vacuum (0·01 mm.), no indication of melting or decomposition was obtained until the temperature reached 200—210°. Rapid decomposition then ensued, the pressure fell to *ca.* 1—2 mm., and a white solid collected. This had m. p. 86°, gave a characteristic Ehrlich reaction (deep violet, turning to blue), and was identical with physostigmol ethyl ether (Stedman, *loc. cit.*).

(ii) *Eserethole methofluoride.* To the methiodide, dissolved in alcohol (6 c.c.) and water (30 c.c.), an aqueous solution of silver fluoride was added, potassium chromate being used as an external indicator. At the end-point the solution was filtered from silver iodide and evaporated to dryness under reduced pressure, leaving a colourless gum (1·4 g.) which later solidified. It was easily soluble in acetone, but was precipitated therefrom (*e.g.*, by light petroleum) as a gum, and was clearly deliquescent.

When heated in a high vacuum (0·001 mm.) the methofluoride (1·05 g.) melted at a bath temperature of 100—105°, and above 120—130° the pressure rose to 0·2—0·4 mm. The temperature was then very slowly increased, and at 140° a distillate began to collect consisting of a colourless liquid mixed with a white solid. Heating was discontinued at 180°, and the product (0·35 g.) divided into two portions. The first (0·2 g.) was dissolved in a boiling alcoholic solution of picric acid (0·16 g.), thus yielding a solid which after three crystallisations gave *l*-eserethole methopicrate (J., 1933, 1474) in glistening red rhombic plates (0·08 g.), m. p. 191° (decomp.). From the mother-liquors a more soluble salt was isolated which ultimately appeared as glistening bronze-yellow leaflets (0·07 g.), m. p. 197—198°. *l*-Eserethole picrate is stated by Polonovski (*loc. cit.*) to have m. p. 133°, whereas Hoshino and Kobayashi (*loc. cit.*, 1935) find 141—142°.

To the remainder of the distillate, after solution in ether and filtration from solid material, methyl iodide was added. A colourless methiodide, m. p. 95—100° (hydrate ?), separated, which was converted into a yellow methopicrate (0·11 g.), m. p. 163—166°. This and the yellow picrate, m. p. 197—198°, above, are being investigated.

Ehrlich's test applied to the distillate remaining in the side-arm of the flask gave a red solution reflecting an olive-green colour.

Except where otherwise stated, the analyses are micro-determinations by Dr. G. Weiler.

Dyson Perrins Laboratory, Oxford University.

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170. *Unsaturated Acids of Natural Oils. Part II. The Highly Unsaturated Acid of the Kernels of* Parinarium Laurinum.

By E. H. Farmer and E. Sunderland.

In a recent paper (*Biochem. J.*, 1935, **29**, 631) one of the authors has described a pair of geometrically isomeric acids (licanic acids) from *Oiticica* oil, in which the octatrienoic skeleton of elæostearic acid is modified by the appearance of a keto-group in the γ-position. Examination of the oil from the kernels of *Parinarium laurinum* has shown that another type of modification of the elæostearic system is to be encountered in vegetable oils, *viz.*, modification by extension of the conjugated system.

The fat extracted from the kernels of *P. laurinum* is a butter-like solid which constitutes about 44% of the kernels. The high refractive index and high iodine value of the (supercooled) liquefied fat point to the presence therein of highly unsaturated components. Saponification of the fat yields a mixture of solid and liquid acids, from which a highly unsaturated acid may be separated by crystallisation from light petroleum. This acid crystallises in rather large plates, m. p. 83·5°, and rapidly becomes transformed by atmospheric oxygen at room temperatures (less rapidly in a refrigerator) into an amorphous material.

When hydrogenated in the presence of platinum, the unsaturated acid takes up four molecular proportions of hydrogen, thereby becoming converted into stearic acid. On oxidation with excess of dilute permanganate solution it yields somewhat less than one

molecular proportion each of azelaic and propionic acids and a quantity of oxalic acid. The acid is clearly, therefore, a straight-chained tetraene acid and there can be little doubt that it may be correctly represented by the formula $CH_3 \cdot CH_2 \cdot [CH\!:\!CH]_4 \cdot [CH_2]_7 \cdot CO_2H$.[*] This being so, the highly unsaturated acid of *P. laurinum* is, so far as the authors are aware, the first *conjugated* acid of the tetraene series to be reported from a vegetable or animal source.

The occurrence of an unsaturated acid of m. p. 85—86° in *P. laurinum* was reported by Tsujimoto and Koyanagi in 1933 (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 110). These authors first assigned the triene constitution $CH_3 \cdot [CH_2]_3 \cdot [CH\!:\!CH]_3 \cdot [CH_2]_6 \cdot CO_2H$, on the ground that the acid yielded sebacic and butyric acids on oxidation; later, however, they withdrew this formula (*loc. cit.*, p. 673) on the ground that the acid had been found to yield azelaic acid and perhaps the half-aldehyde of azelaic acid on ozonolysis. An interesting point reported by Tsujimoto and Koyanagi concerns the capacity of the unsaturated acid to undergo isomerisation by the action of iodine or of light into an acid of m. p. 95—96°, a change analogous to that which can be brought about with elæostearic, licanic, and various other conjugated triene acids, as well as with various members of the carotenoid group.

EXPERIMENTAL.

Isolation of the Highly Unsaturated Tetraene Acid from the Oil of Parinarium laurinum.— The oil had been extracted by petroleum (b. p. 40—60°) from the disintegrated kernels of *P. laurinum* (44% yield) three months before the experiments were carried out. At room temperature it was a butter-like mass which on exposure to the air dried fairly slowly. The refractive index of the (supercooled) liquid oil was high ($n_D^{20°}$ 1·5565).

The butter (10 g.) was refluxed for 3 hours with alcoholic potash made by dissolving potassium hydroxide (5 g.) in a little water and adding alcohol (100 c.c.). The solution of the potassium salts was diluted with 300 c.c. of water, acidified with sulphuric acid, and extracted with ether; the extract was washed with water and dried over sodium sulphate. The bulk of the ether was removed on a steam-bath, and the remainder at reduced pressure without application of heat. The mixture of organic acids obtained was extracted with boiling petroleum (b. p. 40—60°), the insoluble material being rejected. The extract, after being concentrated to about 50 c.c., deposited crystals of a solid acid on cooling. The acid underwent extremely rapid oxidation in the air, apparently with some polymerisation; it had therefore to be handled quickly and preserved in an atmosphere of nitrogen or preferably kept in an open tube resting on solid carbon dioxide in a Dewar vessel. After two or three rapid recrystallisations from petroleum it was obtained in faintly yellow laminæ (2·5—3 g.), m. p. 83·5°.

Hydrogenation. The acid (0·4514 g.) was exhaustively hydrogenated at room temperature in presence of a platinum catalyst. From the amount of hydrogen absorbed (161 c.c. at *N.T.P.*) it was clear that the molecule of the acid contained four double bonds, a conclusion in agreement with the observed high iodine value of the original *Parinarium* oil; repetitions of the hydrogenation confirmed this result.

The hydrogenation product, after being twice crystallised from petroleum, formed shining plates, m. p. 69—70°, which were identified as pure stearic acid (mixed m. p. 69—70°; m. p., and mixed m. p., of methyl ester, 38°).

Oxidation. The acid (2·83 g.) was dissolved in dilute caustic soda solution and oxidised at 0° with 3% permanganate solution. An amount of reagent equivalent to 10 atoms of oxygen was decolorised readily, and the equivalent of a further 6 atoms slowly. The manganese mud was filtered off and extracted several times with boiling water. The filtrate and washings were concentrated to 500 c.c. and acidified with sulphuric acid. The solution was then distilled into sodium carbonate (with suitable addition of water to the distillation vessel) until the aqueous distillate was no longer acid in reaction.

The distillate was evaporated to dryness, cooled in ice, and acidified with concentrated hydrochloric acid. The product was extracted with ether, and the extract dried; on removal

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[*] Actually, representation by one or other of the formulæ $CH_3 \cdot CH_2 \cdot [CH\!:\!CH]_3 \cdot [CH_2]_7 \cdot CH\!:\!CH \cdot CO_2H$, $CH_3 \cdot CH_2 \cdot [CH\!:\!CH]_3 \cdot [CH_2]_7 \cdot [CH\!:\!CH]_2 \cdot CO_2H$, $CH_3 \cdot CH_2 \cdot CH\!:\!CH \cdot [CH_2]_7 \cdot [CH\!:\!CH]_3 \cdot CO_2H$, in which the tetraene system is distributed, would be consistent with the formation of propionic acid and azelaic acid on oxidation. Owing to the small amount of *Parinarium* oil at the disposal of the authors these formulæ could not be formally disproved, but the wide-spread occurrence of the system $:CH \cdot [CH_2]_7 \cdot CO_2H$ in vegetable oils leaves slight probability in favour of these alternative formulæ.

of the solvent under an efficient column there remained a volatile saturated acid, which was carefully fractionated. A low-boiling portion of aqueous acid (b. p. about 100°) was first obtained, but the bulk of acid (0·45 g.) distilled between 130° and 141°. The acid in both fractions was identified as propionic acid (*p*-bromophenacyl ester, m. p. and mixed m. p. 63°). The absence of any significant quantity of another fatty acid was shown by the high degree of purity of the crude phenacyl ester.

The aqueous residue left in the distillation flask (100 c.c.) was extracted with ether. The extract yielded a crystalline acid (1·5 g.), which after recrystallisation from water or benzene melted at 106° and was identified as azelaic acid (mixed m. p. 106°). The diamide of this acid, prepared *via* the chloride, melted at 173° : it agreed in all respects with a specimen of the diamide prepared from authentic azelaic acid.

The sulphuric acid present in the aqueous mother-liquor was precipitated in presence of dilute hydrochloric acid by addition of calcium chloride. The filtrate was then made alkaline with ammonia and boiled, and the precipitated calcium oxalate collected, washed, and estimated volumetrically. Yield of oxalic acid, 0·28 g.

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171. *Unsaturated Acids of Natural Oils. Part III. The Highly Unsaturated Acid of the Kernels of* Parinarium Macrophyllum.

By W. B. BROWN and E. H. FARMER.

THE kernels of the tropical African tree *Parinarium macrophyllum* or *P. Senegalense* of the *Rosaceæ* family yield by petroleum extraction a pale yellow, pleasant smelling, drying oil which remains unchanged for a long time if stored in sealed bottles. The oil constitutes about 70% of the substance of the kernels, or 4% of the nuts. A detailed description of the rather peculiar *P. macrophyllum* nuts and the general character of the oil has recently been published by van Loon (*Rec. trav. chim.*, 1934, **53**, 197), who finds that the oil resembles *Oiticica* oil and yields on saponification about 84% of unsaturated and 10% of saturated acids, also that the mixed acids give on crystallisation from petroleum an unsaturated acid, m. p. 73°, of high refractive index (n_D^{78} 1·5033) and of somewhat indefinite iodine value (187—223).

The present work is concerned with the nature of this unsaturated acid, which van Loon concluded to be an isomeride of elæostearic acid, $CH_3 \cdot [CH_2]_3 \cdot [CH:CH]_3 \cdot [CH_2]_7 \cdot CO_2H$, and probably identical with couepic acid from the oil of *Couepia grandiflora*. Since the present authors have shown that the characteristic, highly unsaturated acid of *Oiticica* oil (the kernel oil of *Licania rigida*), the source of which has been attributed *inter alia* to *Couepia grandiflora* or *C.grandifolia*, is in fact γ-keto-$\Delta^{\theta \kappa \mu}$-octadecatrienoic acid, and not an isomeride of elæostearic acid as the highly unsaturated acid from *C. grandiflora* is believed by van Loon and Steger to be (*Rec. trav. chim.*, 1931, **50**, 936), the identity of the highly unsaturated acid from *P. macrophyllum* remained in doubt. This acid is here shown to be the well-known α-elæostearic acid, m. p. 45·5—46·5°, but since the glyceride of this acid may change even in the course of a few weeks in diffused or dim light, or much more rapidly in sunlight or ultra-violet light (see Part IV), into the β-form of elæostearic glyceride (corresponding to β-elæostearic acid, m. p. 73°), it appears clear that van Loon carried out his experiments mainly with the isomerised or β-form of the glyceride and acid.

The mixed acids obtained by saponification of *P. macrophyllum* oil yielded on fractional crystallisation from petroleum a highly unsaturated acid, m. p. 45·5—46·5°. This acid did not depress the m. p. of authentic α-elæostearic acid, but was different from either of the licanic acids which have been obtained by the authors from *Oiticica* oil. No higher-melting isomeride of this acid could be isolated from freshly extracted *P. macrophyllum* oil.

Confirmation of the identity of the acid, m. p. 45·5—46·5°, with α-elæostearic acid was easily obtainable. The acid gave with maleic anhydride an additive compound identical

with that obtained from authentic α-elæostearic acid derived from Tung oil; moreover it gave on oxidation with permanganate reasonably good yields of valeric, azelaic, and oxalic acids, all of which were fully authenticated.   On hydrogenation in the presence of platinum it took up three molecular proportions of hydrogen, yielding as would be expected pure stearic acid.

There is little doubt that the white stearin-like solid observed by van Loon to separate from *P. macrophyllum* oil in cold weather was α-elæostearin.

Experimental.

Extraction of the Oil.—963 G. of the nuts of *Parinarium macrophyllum*, which corresponded exactly with those described by van Loon (*loc. cit.*), yielded 52 g. of kernels, from which by extraction (Soxhlet) with petroleum (b. p. 40—60°) for 27 hours and removal of the solvent at reduced pressure, 29 g. of a pale yellow, mobile oil of pleasant odour were obtained.   Re-extraction of the residue of the kernels with ether gave a further 8 g. of oil (total yield, 71%). A further batch of 140 g. of kernels on extraction with ether gave 77 g. of 'oil (yield, 55%). Van Loon describes the oil as a colourless liquid, $d_4^{15°}$ 0·8901, $n_D^{70°}$ 1·4741, obtained in 65·2% yield by extraction with petroleum.

Saponification of the Oil and Isolation of the Highly Unsaturated Acid.—40 G. of the oil were refluxed for 7 hours with alcoholic potash (20 g. of potassium hydroxide in a little water, diluted to 200 c.c. with rectified spirits).   The clear brown solution of the potassium soaps was acidified with dilute sulphuric acid, and the precipitated organic acids taken up in 250 c.c. of ether.   The ethereal solution was washed three times with water and dried over sodium sulphate.   To the still liquid mixture of acids obtained by cautious removal of the solvent, 20 c.c. of petroleum (b. p. 40—60°) were added and the resulting solution was cooled in ice.   The crystalline precipitate formed was recrystallised once from petroleum (b. p. 40—60°) and five times from petroleum (b. p. 40—50°); it then melted at 45·5—46·5° and gave no depression of m. p. with authentic α-elæostearic acid (m. p. 45—46°).

Addition Product with Maleic Anhydride.—The pure acid, m. p. 45·5—46·5°, and maleic anhydride in equivalent proportion were heated at about 70° in nitrogen for 1¼ hours.   The solid product was extracted with light petroleum and twice crystallised from this solvent.   The resulting crystals had m. p. 62°, alone or mixed with the addition compound (m. p. 62°) prepared from authentic α-elæostearic acid.

Hydrogenation.—0·06 G. of the acid was hydrogenated with Adams's platinum catalyst. The volume of hydrogen absorbed at 16° and 760 mm. was 14·6 c.c. (13·3 c.c. at *N.T.P.*), corresponding with 2·8 double bonds.   The fully saturated product melted at 67—68°, and at 69—70° after one recrystallisation from methyl alcohol.   On esterification with methyl alcohol the acid yielded its methyl ester, m. p. 38°.   Both the acid and its methyl ester gave no depression of melting point on mixing (respectively) with authentic stearic acid (m. p. 69—70°) and methyl stearate (m. p. 38°).

Oxidation.—1·3 G. of the unsaturated acid were dissolved in 400 c.c. of water containing 0·5 g. of sodium carbonate, and to the cooled and well-stirred solution excess of 4·8% permanganate solution (150 c.c.) was gradually added.   The mixture was kept at room temperature for 48 hours; the unreduced permanganate was then decolorised with sulphurous acid.   The manganese mud was filtered off and extracted six times with boiling water and the aqueous extracts together with the original filtrate were concentrated to about 1¼ l.   The resulting solution was just acidified with hydrochloric acid and then distilled until only 50 c.c. of liquid remained, the distillate dropping into a solution of caustic potash.   A further 150 c.c. of water were added to the liquid in the distillation vessel and distillation was continued until a further 150 c.c. of distillate had passed over into the caustic potash solution.   The distillate was concentrated on a water-bath to 50 c.c., acidified with hydrochloric acid, and extracted four times with ether.   The dried ethereal extract yielded a liquid acid, b. p. 183°, which had the odour of valeric acid (yield, 0·32 g.; 67%).   The *p*-bromophenacyl ester, m. p. 62°, of the acid showed no depression of m. p. when mixed with freshly prepared * *p*-bromophenacyl valerate.

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* It has been repeatedly observed that the m. p. of authentic *p*-bromophenacyl valerate (64°) changes, when the specimen is kept, to a higher m. p. (72°); the nature of the change, which has not been observed with other *p*-bromophenacyl esters, has not been ascertained.   Reid in his latest paper on phenacyl esters (Moses and Reid, *J. Amer. Chem. Soc.*, 1932, **54**, 2101) replaces the lower by the higher m. p. without comment.

From the liquid in the distillation flask an acid crystallised on cooling. This melted at 103—104° and, after one recrystallisation from benzene, at 106°, alone or mixed with azelaic acid. Extraction of the aqueous liquor with ether yielded a further quantity of azelaic acid (total yield, 0·68 g.; 77%).

The aqueous liquor from which the azelaic acid had been removed was freed from residual ether, made alkaline with ammonia, and heated to boiling, calcium chloride solution added, and the precipitated calcium oxalate estimated (yield of anhydrous oxalic acid, 0·23 g.; 27%).

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172. *Canavanine.*

By J. MASSON GULLAND and COLIN J. O. R. MORRIS.

THE amino-acids arginine and canavanine share the distinction of being the only substances known which yield urea directly in the mammalian body. Canavanine, isolated by Kitagawa and his collaborators (*J. Biochem., Japan*, 1929, **11**, 265; *Proc. Imp. Acad. Japan*, 1929, **5**, 380) from the jackbean (*Canavalia ensiformis*), has the molecular formula $C_5H_{12}O_3N_4$, and the problem of its constitution has chiefly been studied with the simpler amino-acid canaline, $C_4H_{10}O_3N_2$, which is formed together with urea by the fission of canavanine with the liver enzyme canavanase. The constitution (I) assigned to canaline by Kitagawa is largely based on its quantitative fission (Kitagawa and Monobe, *J. Biochem., Japan*, 1933, **18**, 333) by catalytic reduction to ammonia and a substance which was regarded as identical with synthetic α-amino-γ-hydroxybutyric acid (Fischer and Blumenthal, *Ber.*, 1907, **40**, 106; Sørensen and Andersen, *Z. physiol. Chem.*, 1908, **56**, 250). A comparison of the properties of this material and its derivatives with those of the synthetic compound does indeed suggest a close relationship, but does not for the following reasons give proof of the identity : certain minor discrepancies in properties may be detected, no direct comparison of the substances from natural and synthetic sources was made, and the probability that the α-amino-γ-hydroxybutyric acid obtained under such conditions from optically active canaline would also be active was apparently not considered by the Japanese authors.

$$NH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$$
(I)

$$NH_2 \cdot C(:NH) \cdot NH \cdot O \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$$
(III.)

$$NH_2 \cdot CH_2 \cdot CH(OH) \cdot CH(NH_2) \cdot CO_2H$$
(II)

$$NH_2 \cdot C(:NH) \cdot NH \cdot CH_2 \cdot CH(OH) \cdot CH(NH_2) \cdot CO_2H$$
(IV)
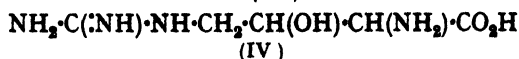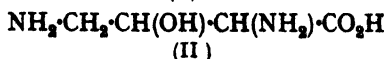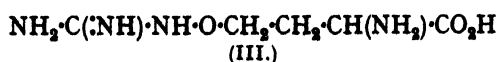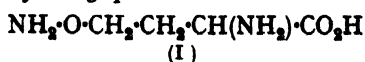
The structure (I)—a hydroxylamine derivative—is so unexpected in the group of amino-acids as to require confirmation, and our practical interest in the problem was also aroused by the possibility that canaline might be the isomeric αγ-diamino-β-hydroxybutyric acid (II), since we had recently confirmed (*J.*, 1934, 1644) that such α-amino-β-hydroxy-acids—apart from serine—may occur in nature by preparing from casein β-hydroxyglutamic acid (Dakin, *Biochem. J.*, 1918, **12**, 290), the re-isolation of which had for long baffled other workers.

No complete structure for canavanine has yet been proposed, and Kitagawa and Yamada (*J. Biochem., Japan*, 1932, **16**, 339) have stated that " it cannot be considered likely that the guanidine group $NH_2 \cdot C(:NH) \cdot NH$ is present in canavanin, but it is possible to suggest that canavanin is more nearly related to guanidine derivative than to ureide derivative." Nevertheless the presence of a guanidine group would express most readily the properties of canavanine—its basic character, its fission into urea and an amino-compound, and the interaction of two only of its four nitrogen atoms with nitrous acid in Van Slyke determinations of amino-nitrogen (Kitagawa and Yamada, *loc. cit.*). The introduction of the guanidine group into (I) and (II) would lead, therefore, to (III) and (IV) as possible structures for canavanine. Our investigations have dealt solely with

canavanine, not with canaline, in view of the desirability of working with a material which has not been subjected to the action of the complex battery of enzymes of the liver, and a method is now described which is more practicable for the isolation of canavanine than those hitherto recorded.

Oxidation with chloramine-T is the most effective process for the detection of β-hydroxy-amino-acids, since it yields α-hydroxy-aldehydes. Oxidation of canavanine in this way, followed by precipitation of carbonyl compounds with *p*-nitrophenylhydrazine, yielded the *p*-nitrophenylosazones of glyoxal and tartronic semialdehyde (V). The glyoxal fragment was presumably formed as the result of decarboxylation, since its osazone alone was obtained when the oxidation and osazone formation were effected in acetic acid, whereas the osazone of (V) alone was isolated after the reactions had been carried out in dilute hydrochloric acid.

$$CO_2H \cdot CH(OH) \cdot CHO \qquad CO_2H \cdot CH(OH) \cdot CH(NH_2) \cdot CO_2H \qquad CH_2Br \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$$
$$\text{(V.)} \qquad\qquad\qquad \text{(VI.)} \qquad\qquad\qquad\qquad \text{(VII.)}$$
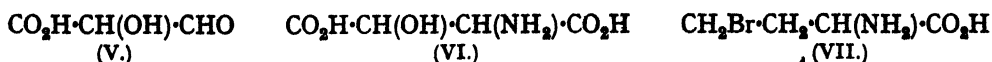
These facts appeared at first to strengthen the possibility that canavanine might be (IV), since Dakin (*Biochem. J.*, 1919, **13**, 419) obtained tartronic semialdehyde *p*-nitrophenylosazone by the same method from hydroxyaspartic acid (VI); in the present case oxidation of the guanidino-methylene group to carboxyl might occur. This possibility, however, was not supported by the observation that the solution obtained from the chloramine-T oxidation did not rotate polarised light, as would have been expected if it contained tartronic semialdehyde from (IV). This might have been due to racemisation or internal oxidation-reduction to the corresponding ketonic primary alcohol, though this seems improbable from the work of Berl and Fodor (*Z. ges. Schiess.-Sprengstoffw.*, 1910, **5**, 296). Alternatively, the osazones of glyoxal and (V) might have resulted from the oxidation products of aspartic acid, formed by oxidation of (III) at the $NH_2 \cdot C(:NH) \cdot NH \cdot O \cdot CH_2$ group; aspartic acid is known to yield glyoxal under these conditions (Dakin, *Biochem. J.*, 1917, **11**, 79).

The action of hot halide acids on canavanine seemed to offer a method of distinguishing between (III) and (IV), since O-ethers of hydroxylamine readily yield the alkyl halide and hydroxylamine, whereas arginine is remarkably stable to this treatment; (III) may be regarded as an O-ether of a N-substituted hydroxylamine; and (IV) is a hydroxylated, lower homologue of arginine. Hot concentrated hydrobromic acid converted canavanine into ammonia, guanidine, and a substance which must be regarded as α-amino-γ-butyro-lactone hydrobromide in view of its properties. This substance could not be completely separated from admixed ammonium bromide and sodium bromide (from sodium carbonate used in the preparation), but when heated again with concentrated hydrobromic acid it yielded optically inactive *γ-bromo-α-aminobutyric acid hydrobromide* (as VII), identical with a specimen prepared by the same method from synthetic α-aminobutyrolactone (Fischer and Blumenthal, *Ber.*, 1907, **40**, 106). The racemisation at the α-carbon atom of canavanine which occurs during the treatment is paralleled by the racemisation of arginine by hot concentrated sulphuric acid (Kutscher, *Z. physiol. Chem.*, 1901, **32**, 478; Reisser, *ibid.*, 1906, **49**, 222).

These results prove canavanine to have the structure (III) and confirm the conclusions of Kitagawa and Monobe as to the structure of canaline.

<div align="center">EXPERIMENTAL.</div>

Preparation of Canavanine.—Jackbean meal was freed from oil by extraction (Soxhlet) for 24 hours with acetone. The oil-free, air-dried meal (200 g.) was extracted twice with 50% (by weight) aqueous ethyl alcohol (1 l.) on a shaker for 1 hour. The combined extracts were concentrated under reduced pressure to a syrup, which was poured into vigorously stirred, absolute alcohol (15—20 vols.). Next day the alcohol was decanted from the sticky solid; this was dissolved in warm water (4 parts) and filtered slowly into mechanically stirred, cold absolute alcohol (15 vols.), and the mixture kept at 0° till next day. For the success of this precipitation it is essential to make the addition slowly and to use enough alcohol. The crude canavanine which had separated was collected, washed with absolute alcohol (when dried under

reduced pressure, the yield from 1·5 kg. was 180 g.), and dissolved in water (500 c.c.). The solution was acidified with dilute sulphuric acid and mixed with flavianic acid (250 g.) in water (400 c.c.). The mixture was kept at 0° for 12 hours, and the crystalline flavianate was collected, washed with dilute flavianic acid solution, and recrystallised twice from water. This removed a small amount of a sparingly soluble, deep red flavianate, which was discarded; the canavanine flavianate ultimately obtained formed yellow needles, m. p. 212° (Kitagawa and Yamada record that the flavianate becomes semi-fluid at 190—192° and melts with decomposition at 210—215°).

Kitagawa and his collaborators continued the isolation of canavanine by way of the picrate (m. p. 163—164°, Kitagawa and Yamada; m. p. 155—158°, Kitagawa and Tomita). We have prepared a picrate, m. p. 220°, from the neutralised hydrochloride of the pure amino-acid, but it is rather readily soluble in water, and we have been unable to follow the isolation used by Kitagawa owing to lack of experimental details of procedure.

Various methods of decomposing the flavianate—decomposition by concentrated hydrochloric acid, adsorption of the flavianic acid with wool in acid suspension (cf. Mueller, *Z. physiol. Chem.*, 1932, 209, 207), decomposition by electrodialysis, precipitation of the flavianic acid as lead salt with lead oxide—proved unsuccessful or unsatisfactory, and the following procedure was finally adopted. A hot aqueous solution of the flavianate was mixed with a slight excess of warm baryta solution, the mixture cooled, and the barium flavianate collected and extracted twice with boiling water. The filtrate and washings were combined and freed from barium ions by titration with 0·1N-sulphuric acid, sodium rhodizonate being used as an external indicator (Giblin, *Analyst*, 1933, 58, 752). The barium sulphate was removed and extracted with boiling water and the combined filtrate and washings were concentrated to small volume. The solution, still yellow, was mixed with excess of a concentrated aqueous solution of rufianic acid (Zimmermann, *Z. physiol. Chem.*, 1930, 188, 180) and left at 0° for 24 hours. The crystalline rufianate, recrystallised from hot water, formed deep red, spherical aggregates (unmelted below 350°), which were dissolved in hot water and mixed with excess of warm baryta solution. The mixture was cooled and filtered from barium rufianate, and the almost colourless filtrate was freed from barium ions by titration with 0·1N-sulphuric acid and sodium rhodizonate. The barium sulphate, which carried down the last traces of colour, was collected and extracted with boiling water, and the colourless solution was concentrated to small volume under reduced pressure and poured into absolute alcohol (15 vols.). No immediate precipitation occurred, but after remaining over-night at 0°, a good yield of crystalline canavanine, m. p. 184°, had separated and a further amount was obtained by concentrating the mother-liquor. The canavanine formed colourless irregular crystals, m. p. 184°, $[\alpha]_D^{20}$ + 7·9° in water (c = 3·2%) (Found : C, 34·2; H, 6·9; N, 30·7. Calc. for $C_5H_{12}O_3N_4$: C, 34·1; H, 6·8; N, 31·8%). Kitagawa and Yamada give m. p. 182—183° and $[\alpha]_D$ + 8·09°. It gave the characteristic colour reaction with irradiated sodium nitroprusside solution, a positive ninhydrin, and a negative Sakaguchi reaction. The failure to give the Sakaguchi reaction, characteristic of the guanidine group of arginine, is explicable on Poller's observation (*Ber.*, 1926, 59, 1927) that, in the case of unsubstituted guanidine radicals, a positive test is obtained only when the radical is united directly to a carbon atom which is essentially part of an alkyl group.

Oxidations with Chloramine-T.—(i) *In dilute acetic acid.* A mixture of a saturated aqueous solution of chloramine-T (5·1 g.) and canavanine (0·92 g.) in water (10 c.c.), previously neutralised with acetic acid, was kept for ¼ hour at room temperature, warmed at 60° for 1 hour, cooled, and filtered from *p*-toluenesulphonamide. The filtrate was heated on the water-bath for 1½ hours with *p*-nitrophenylhydrazine (3 g.) in alcoholic acetic acid and cooled. The precipitate was collected, extracted with hot nitrobenzene to remove a small amount of soluble material which was not an osazone (no blue colour with alkali), and recrystallised from pyridine. It formed scarlet needles, m. p. 309° alone or mixed with authentic glyoxal-*p*-nitrophenylosazone, and gave the blue coloration with sodium hydroxide characteristic of *p*-nitrophenylosazones.

(ii) *In dilute hydrochloric acid.* A mixture of chloramine-T (10 g.) suspended in water (25 c.c.) and canavanine (2 g.) dissolved in water (4 c.c.), previously neutralised with hydrochloric acid, was kept at room temperature for 1 hour, cooled, and filtered. The filtrate was optically inactive and remained so after being warmed at 60° for ¼ hour. It was heated with *p*-nitrophenylhydrazine (6 g.) in dilute alcoholic hydrochloric acid for 1 hour, and the precipitate was collected, washed with water and alcohol, and extracted with boiling nitrobenzene to remove a small amount of soluble material which was not an osazone. The insoluble residue of tartronic aldehyde *p*-nitrophenylosazone crystallised from much nitrobenzene in red needles, m. p. 302° alone or mixed with an authentic specimen (m. p. 302°) (Dakin, *Biochem. J.*, 1919,

12, 398) (Found : N, 22·6. Calc. for $C_{15}H_{14}O_6N_2$: N, 22·6%). It gave a royal-blue colour when dissolved in acetone and treated with sodium hydroxide solution.

In connection with the constitution of canavanine, it is noteworthy that in both the experiments described above the solution became deep yellow during the oxidation with chloramine-T. Guanidine behaved similarly under the same conditions, whereas in experiments with methylguanidine and arginine, in which the guanidine group is directly united to carbon, the liquid remained colourless. Methylguanidine, moreover, yielded much methylamine, showing that the carbon–nitrogen linkage is not broken by the oxidation.

Action of Mineral Acids on Canavanine.—Preliminary experiments showed that canavanine is rapidly decomposed—no reaction with irradiated nitroprusside—by boiling 25% sulphuric acid, whereas it was recovered unchanged after being heated under reflux for 3 hours with 20% hydrochloric acid.

(i) *Dilute hydrobromic acid.* A solution of canavanine (0·2 g.) in hydrobromic acid (6 c.c., *d* 1·3) and water (3 c.c.) was heated for 3 hours in a sealed tube at 150°. The contents of the tube were evaporated to dryness under reduced pressure and dissolved in water. The solution, which gave a pronounced ninhydrin reaction but no coloration with irradiated nitroprusside, contained ammonia and urea, isolated as dixanthylurea, but gave no precipitate of the sparingly soluble guanidine picrate when neutralised and mixed with picric acid.

A parallel experiment under similar conditions with guanidine yielded ammonia and a small amount of urea, but only 12·5% of the guanidine was recovered unchanged as picrate.

(ii) *Concentrated hydrobromic acid.* A solution of canavanine (1·3 g.) in 60% hydrobromic acid (25 c.c., *d* 1·7) was heated in a sealed tube for 5 hours at 160°. The contents of the tube were evaporated to dryness under reduced pressure, and the residue was dissolved in water, neutralised to litmus with sodium carbonate, and mixed with an excess of a cold saturated aqueous solution of picric acid. The mixture was kept for 3 hours at 0°, and the guanidine picrate (18·8%), m. p. 315°, was collected, washed with water, and dried at 100°. After re-crystallisation from water, it melted at 318° alone or mixed with an authentic specimen.

The filtrate from the picrate was acidified with hydrobromic acid and freed from picric acid by extraction with benzene. The aqueous layer was evaporated to dryness under reduced pressure ; the product gave a pronounced ninhydrin reaction, but also contained ammonium and sodium bromides. It was repeatedly extracted with a cold mixture of equal parts of alcohol and chloroform, but scarcely any material dissolved. There can be little doubt that this insoluble product consisted essentially of α-aminobutyrolactone hydrobromide, since an authentic specimen gave a strongly positive ninhydrin reaction, was insoluble in a mixture of alcohol and chloroform, and yielded γ-bromo-α-aminobutyric acid hydrobromide when heated with hydrobromic acid. The crude lactone hydrobromide was heated with 60% hydrobromic acid (20 c.c.) in a sealed tube for 5 hours at 160°, and the contents of the tube were evaporated to dryness and extracted with cold ethyl alcohol–chloroform (1 : 3), which dissolved all the material giving the positive ninhydrin reaction, and left undissolved sodium bromide and most of the ammonium bromide. The filtered solution was freed from solvent and again extracted with alcohol–chloroform. The solution from this extract was evaporated, and the residue dissolved in dilute hydrobromic acid and concentrated under reduced pressure to a very small volume. The oily mass solidified to a crystalline mass, which was pressed on porous tile and crystallised twice from alcohol–chloroform. The resulting γ-*bromo-α-aminobutyric acid hydrobromide* formed fine colourless needles, m. p. 164° alone or mixed with a synthetic specimen (Found : C, 18·5 ; H, 3·6 ; Br, 60·9. $C_4H_8O_2NBr,HBr$ requires C, 18·3 ; H, 3·4 ; Br, 60·8%). An 8·2% aqueous solution showed no optical activity.

γ-*Bromo-α-aminobutyric Acid Hydrobromide.*—A solution of α-aminobutyrolactone hydrobromide (1 g.) (Fischer and Blumenthal, *loc. cit.*) in 60% hydrobromic acid (6 c.c.) was heated in a sealed tube at 160° for 5 hours. The contents of the tube were concentrated to small volume under reduced pressure and the crystalline mass was extracted with absolute alcohol, to remove traces of insoluble material. The residue obtained by evaporation of the alcohol was twice crystallised by precipitation from a very concentrated solution in hot alcohol with chloroform. γ-Bromo-α-aminobutyric acid hydrobromide formed fine square-ended needles, m. p. 164° (decomp.), which gave a strong ninhydrin reaction (Found : C, 18·4 ; H, 3·5 ; N, 4·9 ; Br, 60·3. Calc. for $C_4H_8O_2NBr,HBr$: C, 18·3 ; H, 3·4 ; N, 5·3 ; Br, 60·8%). It dissolved readily in water, ethyl and methyl alcohols, and glacial acetic acid, was less soluble in acetone, and insoluble in chloroform.

173. *Synthetic Uses of* as-*Octahydrophenanthrene. Part I.*

By J. W. COOK and G. A. D. HASLEWOOD.

as-OCTAHYDROPHENANTHRENE is readily available in quantity by the method of Cook and Hewett (J., 1933, 1098) and furnishes a convenient starting point for the synthesis of more complex hydroaromatic compounds, some of which are now described.

By analogy with tetralin it was anticipated that Friedel–Crafts reactions with acyl chlorides would lead to substitution at position 6 or 7 of the octahydrophenanthrene ring system (I). Reaction with succinic anhydride and aluminium chloride in nitrobenzene led to a crystalline keto-acid as the only product which could be isolated, and this was shown to have structure (II) by oxidation to 6-as-*octahydrophenanthroic acid*, followed by dehydrogenation to 3-phenanthroic acid. The position of substitution in the Friedel–Crafts reaction thus corresponds to that in phenanthrene itself, which gives mainly the 3-compounds with acyl chlorides (Mosettig and van de Kamp, *J. Amer. Chem. Soc.*, 1930, **52**, 3704; Haworth and Mavin, J., 1933, 1012; Cook and Haslewood, J., 1934, 428).

β-6-as-*Octahydrophenanthroylpropionic acid* (II) * was reduced by Clemmensen's method to γ-6-as-*octahydrophenanthrylbutyric acid* (III), which was smoothly cyclised by 88% sulphuric acid to 5-*ketododecahydro*-1 : 2-*benzanthracene* (IV). This passed, on Clemmensen reduction, into the corresponding *dodecahydro*-1 : 2-*benzanthracene*, isomeric with that already described (Cook and Hewett, J., 1934, 375).

(I.)   (II.)   (III)

(IV.)   (V.)   (VI)
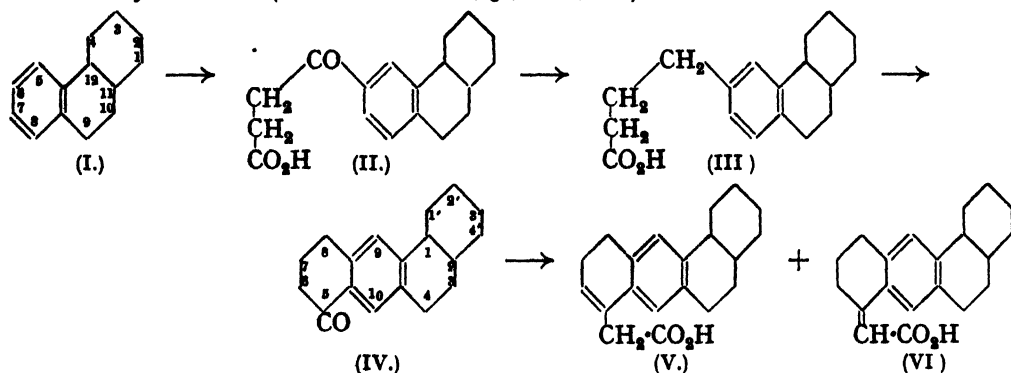
The tetracyclic ketone (IV) had a much higher solubility than the 5-keto-5 : 6 · 7 · 8-tetrahydro-1 : 2-benzanthracene of Haworth and Mavin (*loc. cit.*), and probably on this account the dodecahydro-ketone readily condensed with ethyl bromoacetate under suitable conditions, whereas the tetrahydro-ketone did not. This Reformatsky reaction with (IV) led to a mixture of unsaturated *acids* (V and VI), one of which was isolated in the pure state. This, or the mixture of the two, could be hydrogenated with palladium-black to the crystalline *dodecahydro*-1 : 2-*benzanthrylacetic acid*, which was cyclised by sulphuric acid to *ketododecahydrocholanthrene* (VII). This pentacyclic ketone was reduced by amalgamated zinc and hydrochloric acid to *dodecahydrocholanthrene* (VIII), which was dehydrogenated by platinum-black at 300° to cholanthrene, identical with that obtained by two other methods (this vol., pp. 667, 770).

(VII.)   (VIII.)   (IX)
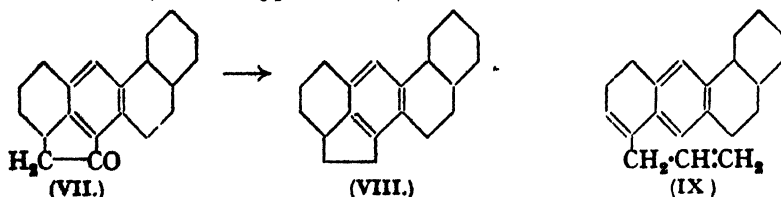
* To avoid the use of unnecessarily cumbersome series of figures, the positions of hydroaromatic hydrogen atoms are not denoted in the names of compounds. The systems of numbering which are intended to be used are given in formulæ (I) and (IV).

In an attempt to obtain the dodecahydro-1 : 2-benzanthryl-5-acetic acid in better yield, the tetracyclic ketone (IV) was condensed with allylmagnesium bromide, and the crude carbinol dehydrated. The resulting hydrocarbon (probably IX), formed in good yield, was treated with sodium and boiling amyl alcohol, by which means it was hoped to reduce the nuclear double bond, with subsequent oxidation to the desired acid. This project could not be realised, as the hydrocarbon (IX) was unaffected by sodium and amyl alcohol (compare Haslewood and Roe, this vol., p. 465). When this hydrocarbon was heated with platinum-black at 300°, dehydrogenation of the ring system was accompanied by hydrogenation of the side chain, so that the product was 5-n-*propyl*-1 : 2-*benzanthracene*. It thus seems likely that the tetracyclic ketone (IV) will be serviceable for the synthesis of other higher homologues of 1 : 2-benzanthracene with substituents at position 5, for which purpose 5-keto-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene was unsuitable (Cook, J., 1933, 1593). In view of the marked carcinogenic activity of 5-methyl-1 : 2-benzanthracene (Barry, Cook, Haslewood, Hewett, Hieger, and Kennaway, *Proc. Roy. Soc.*, 1935, *B*, 117, 318) a study of such compounds should be profitable.

There is as yet no evidence concerning the stereochemical configuration with respect to the points of attachment of the two condensed hydroaromatic rings present in many of the compounds now described.

EXPERIMENTAL.

* Denotes microanalysis by Dr. A. Schoeller. † Denotes microanalysis by Dr. G. Weiler.

β-6-as-*Octahydrophenanthroylpropionic Acid* (II).—The *as*-octahydrophenanthrene used in these experiments was prepared by F. Goulden by the action of aluminium chloride on β-phenylethyl-Δ¹-*cyclo*hexene in carbon disulphide (6 hours at room temperature). The distilled hydrocarbon (57 g.), cooled to 0°, was added during ¼ hour to a solution of aluminium chloride (80 g.) and succinic anhydride (33 g.) in nitrobenzene (240 c.c.), the whole being cooled in a freezing mixture. The dark red solution was kept at 0° for 5 hours and then poured on ice and hydrochloric acid. The whole was extracted with ether, and the acidic reaction products removed from the extract by agitation with 10% potassium hydroxide solution. After washing with ether, the alkaline extract was acidified, and the liberated acids extracted with ether. The brown oil remaining after removal of the ether became crystalline when digested with methyl alcohol. Recrystallisation from benzene–ligroin gave colourless crystals (27 g.), m. p. 134—137°. For complete purification, the semicarbazone was prepared (m. p. 185—187ᵇ, decomp.), and hydrolysed by a boiling saturated solution of oxalic acid. β-6-as-*Octahydrophenanthroylpropionic acid* (II) crystallised from glacial acetic acid in colourless prisms, m. p. 140—141° (Found : C, 75·4; H, 8·0. $C_{18}H_{22}O_3$ requires C, 75·5; H, 7·75%). The mother-liquors from which the crude acid had been separated contained considerable amounts of other substances, but no pure isomeride could be isolated. Repeated crystallisation of the semicarbazones gave a fraction, m. p. 144—146° (decomp.), but the product of hydrolysis would not crystallise.

6-as-*Octahydrophenanthroic Acid*.—The keto-acid (II) (2 g.) was oxidised with a dilute alkaline solution of potassium permanganate (2·2 g.) at room temperature. The product, crystallised from methyl alcohol (charcoal), acetic acid, and then *cyclo*hexane, formed colourless prisms, m. p. 226—228° (slight decomp.) (*Found : C, 78·2; H, 7·8. $C_{15}H_{18}O_2$ requires C, 77·9; H, 7·85%). Dehydrogenation of this *octahydrophenanthroic acid* (0·4 g.) with selenium (1 g.) at 280—300° (24 hours) gave 3-phenanthroic acid, m. p. 268—270°, identified by direct comparison with an authentic sample.

γ-6-as-*Octahydrophenanthrylbutyric Acid* (III).—The keto-acid (II) (15 g.) was boiled for 6 hours with amalgamated zinc (from 45 g. of granulated zinc) and hydrochloric acid (22·5 c.c. of concentrated acid and 45 c.c. of water), a further 7·5 c.c. of concentrated acid being added at the end of each hour. The product was extracted with ether, the extract cautiously washed with sufficient sodium carbonate solution to remove hydrochloric acid, and the dried ethereal solution distilled. γ-6-as-*Octahydrophenanthrylbutyric acid* (12·2 g.), b. p. 198°/0·15 mm., was crystallised from light petroleum, then from aqueous alcohol, and finally from light petroleum, forming small, colourless, hexagonal prisms, m. p. 81—83° (Found : C, 79·1; H, 9·1. $C_{18}H_{24}O_2$ requires C, 79·3; H, 8·9%).

5-*Ketododecahydro*-1 : 2-*benzanthracene* (IV).—The reduced acid (III) (9 g.) was heated at 100° for an hour with a mixture of concentrated sulphuric acid (36 c.c.) and water (9 c.c.).

After dilution with water, the product was extracted with ether, washed free from acid, and the residue remaining after removal of the ether was recrystallised from methyl alcohol. The tetracyclic *ketone* (IV) (0·5 g.) formed colourless needles, m. p. 120—121°, from ligroin (Found: C, 85·0; H, 8·8. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%).

Dodecahydro-1 : 2-*benzanthracene* was obtained by reduction of this ketone by Clemmensen's method, the product being distilled at 180°/0·2 mm. and then recrystallised from light petroleum. It formed colourless needles, m. p. 87—88° (*Found : C, 89·5; H, 9·95. $C_{18}H_{24}$ requires C, 89·9; H, 10·1%).

Dodecahydro-1 : 2-*benzanthryl-5-acetic Acid*.—Ethyl bromoacetate (3·8 c.c.) was added to a mixture of 5-ketododecahydro-1 : 2-benzanthracene (IV) (8·7 g.), pure benzene (25 c.c.), anhydrous ether (25 c.c.), and magnesium (0·82 g.). After addition of a trace of iodine a vigorous reaction set in on warming, and the whole boiled spontaneously for 20 minutes. The mixture was kept at room temperature for 20 hours, and then treated again with magnesium and ethyl bromoacetate, exactly as described above. After a further 20 hours at room temperature the reddish-brown solution was treated with dilute hydrochloric acid, the solvents removed from the washed ethereal extract, and the residue hydrolysed by boiling alcoholic potassium hydroxide (100 c.c. of 10% solution). After extraction of the acidic products, 3—4 g. of unchanged ketone were isolated. The acid fraction was purified by esterification (methyl-alcoholic hydrogen chloride), distillation of the esters (b. p. 195—212°/0·2 mm.; 2·6 g.), followed by hydrolysis. When the crude resinous acids were digested with *cyclo*hexane, a crystalline unsaturated *acid* (V or VI) was isolated in small yield. This crystallised from benzene in small colourless plates, m. p. 226—232° (efferv.) (†Found : C, 81·2; H, 8·2. $C_{20}H_{24}O_2$ requires C, 81·0; H, 8·2%).

The resinous mixture of acids from which this crystalline material had been isolated (4·8 g., from several batches), purified as described above, was hydrogenated by shaking its ethereal solution (100 c.c.) for 3 hours with hydrogen and palladium-black (1·2 g.). The resulting *dodecahydro*-1 : 2-*benzanthryl-5-acetic acid* crystallised from benzene–ligroin in colourless microscopic needles (2 g.), and had m. p. 163—165° after several recrystallisations (*Found : C, 80·7; H, 8·9. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·8%). The same acid resulted from the hydrogenation of the crystalline unsaturated acid (V or VI).

By heating with platinum-black at 300° for 9 hours, both dodecahydrobenzanthrylacetic acid and the mixture of unsaturated acids (V and VI) suffered dehydrogenation and decarboxylation, the resulting 5-methyl-1 : 2-benzanthracene being identified by direct comparison with an authentic sample (Cook, J., 1933, 1596). An attempt was made to avoid decarboxylation by heating the methyl ester of dodecahydrobenzanthrylacetic acid with selenium at 290—300°. Hydrolysis gave a small amount of an acid which, after sublimation in a vacuum, was purified through its dark red picrate (m. p. 170—173°). Picric acid was removed by reduction with stannous chloride, and the product was crystallised from *cyclo*hexane. This substance, m. p. 160—162°, was undoubtedly 1 : 2-benzanthryl-5-acetic acid, but the amount was too small for further purification.

Ketododecahydrocholanthrene (VII).—A mixture of dodecahydro-1 : 2-benzanthryl-5-acetic acid (2 g.), concentrated sulphuric acid (8 c.c.), and water (2 c.c.) was heated at 100° for an hour. The resulting *ketone* (VII), washed free from acid, crystallised from methyl alcohol in long colourless needles (1·3 g.) which, after recrystallisation from ligroin, had m. p. 114—116° (*Found : C, 85·7; H, 8·9. $C_{20}H_{24}O$ requires C, 85·65; H, 8·6%). This ketone (1·2 g.) was reduced by Clemmensen's method to *dodecahydrocholanthrene* (VIII), which, after distillation, crystallised from alcohol–ligroin in small colourless needles, m. p. 62—63° (*Found : C, 90·3; H, 9·8. $C_{20}H_{26}$ requires C, 90·2; H, 9·8%).

Cholanthrene.—The foregoing hydrocarbon (VIII) (0·2 g.) was heated in an atmosphere of carbon dioxide at 290—310° for 7 hours with platinum-black (50 mg.). Cholanthrene, m. p. 167·5—168·5° (picrate, m. p. 167—168·5°), was obtained in good yield, being purified by vacuum sublimation and then recrystallisation from benzene–alcohol.

5-n-*Propyl*-1 : 2-*benzanthracene*.—Allylmagnesium bromide (compare Gilman and McGlumphy, *Bull. Soc. chim.*, 1928, **43**, 1322) was prepared by addition during 45 minutes, with continuous agitation, of a solution of allyl bromide (6 g.) in anhydrous ether (28 c.c.) to magnesium turnings (7·2 g.), suspended in ether (20 c.c.). The Grignard solution, decanted from the excess of magnesium, was treated with 5-ketododecahydro-1 : 2-benzanthracene (IV) (6·35 g.), suspended in ether (80 c.c.). After an hour at room temperature, the mixture was boiled for 2 hours and then kept at room temperature for 20 hours. The crude resinous carbinol, isolated after decomposition with ice and ammonium chloride, was dehydrated by

heating at 155—160° for 10 minutes. The resulting hydrocarbon (IX) was twice distilled, and had b. p. 174°/0·1 mm. The bromine absorption value (pyridine sulphate dibromide reagent) was in agreement with that required by formula (IX), and was completely unaffected by two treatments with sodium in boiling amyl alcohol.

This hydrocarbon (IX) (1·5 g.) was heated with platinum-black (0·4 g.) for 9 hours at 295—300° in an atmosphere of carbon dioxide. The resulting 5-n-*propyl*-1 : 2-*benzanthracene* was purified by crystallisation from benzene of its dark red *picrate*, m. p. 131·5—132·5° (†Found : N, 8·5. $C_{21}H_{18}.C_6H_3O_7N_3$ requires N, 8·4%). The regenerated hydrocarbon crystallised from alcohol in colourless fluorescent needles, m. p. 91—91·5° (†Found : C, 93·3; H, 6·7; *M*, Rast method, 280. $C_{21}H_{18}$ requires C, 93·3; H, 6·7%; *M*, 270), and was oxidised by sodium dichromate (5 parts) in boiling acetic acid to 5-n-*propyl*-1 : 2-*benzanthraquinone*, which, crystallised from alcohol and then from ligroin, formed orange-yellow needles, m. p. 104—105·5° (†Found : C, 83·8; H, 5·3. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·4%).

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174. *A Convenient Synthesis of Cholanthrene.*

By J. W. COOK and G. A. D. HASLEWOOD.

THE two synthetic methods by which cholanthrene has been obtained (this vol., pp. 667, 767) provide complete proof of the structure of the product, but they are very tedious and not well adapted to the preparation of a supply of material for biological investigation. The method now described is more suitable for this purpose.

Evidence was obtained by Salkind (*Ber.,* 1934, **67**, 1031) that the β-bromine atom of 1 : 2-dibromonaphthalene is the more reactive towards magnesium. It thus seemed possible that the monomagnesio-compound would react with α-hydrindone to give, after dehydration and reduction, the bromo-compound (I). In order to enhance the reactivity of the β-halogen atom we employed 1-bromo-2-iodonaphthalene, and we also used Grignard's device (*Compt. rend.,* 1934, **198**, 625) of adding a molecule of ethylmagnesium bromide to facilitate the formation of the Grignard compound. Unfortunately, the product of interaction of the resulting magnesio-derivative with α-hydrindone was a bromine-free compound, probably a cyclic oxide, which gave analytical figures in agreement with $C_{19}H_{14}O$.

As an alternative route to the desired bromo-compound (I) we studied the bromination of 1-β-naphthylhydrindene. It was anticipated that bromination of the naphthalene nucleus would take place at the required position, and there was also a likelihood of substitution in the hydrindene system. This proved to be the case. A resinous mixture of bromo-compounds was obtained, from which compounds brominated in the five-membered ring were removed by the procedure described in the experimental section. The product was then combined with magnesium, and the resulting Grignard solution treated with carbon dioxide. This gave a resinous mixture of acids, 40% of which was isolated as a crystalline compound which proved to be β-1-*hydrindyl-α-naphthoic acid* (II). Dehydration with ice-cold sulphuric acid led to an anthrone-like product (III), which was reduced in the crude state with zinc dust and alkali, cholanthrene being formed in good yield.

(I.)   (II.)   (III.)
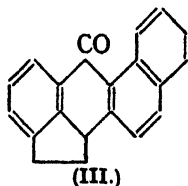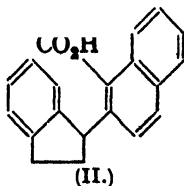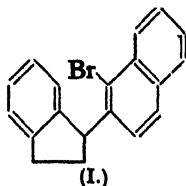
EXPERIMENTAL.

1-β-*Naphthylhydrindene.*—This was obtained by hydrogenation (palladium-black) of the indene resulting from interaction of α-hydrindone and β-naphthylmagnesium bromide. The

yield of the indene, was 57%. The same two compounds were obtained by v.Braun, Manz, and Reinsch (*Annalen*, 1929, **468**, 296), who stated that they used α-naphthyl bromide, but it is clear from the text of their paper that they really used the β-compound. Our indene had m. p. 97° and the hydrindene 52—53° (Found : C, 93·1; H, 6·6. Calc. : C, 93·4; H, 6·6%). The above authors give 88° and 47°, respectively, for the m. p.'s of these two compounds.

β-1-*Hydrindyl-α-naphthoic Acid* (II).—Bromine (3·7 c.c.), diluted with carbon disulphide (30 c.c.), was added to a solution of the naphthylhydrindene (18·7 g.) in carbon disulphide (30 c.c.), a little aluminium chloride having been introduced as a halogen carrier. The mixture was kept in the dark at room temperature for 7 hours. After removal of the solvent, the resulting yellow oil was boiled with anhydrous pyridine (50 c.c.) for an hour. The dark-coloured solution was treated with excess of dilute acid and extracted with benzene, and the extract twice agitated with 80% sulphuric acid. Distillation of the product gave an orange viscous liquid (17 g.), b. p. 180—195°/0·2 mm. This product was mixed with magnesium turnings (2·4 g.) and anhydrous ether (50 c.c.), ethyl bromide (3·8 c.c.) in ether (20 c.c.) being then added to promote interaction with magnesium. After an hour's boiling, the whole was cooled in ice, and treated for 6 hours with a slow stream of dry carbon dioxide. After decomposition with dilute hydrochloric acid, the acidic products were isolated by extraction with dilute alkali. The reprecipitated resinous acids (10 g.) were shaken with hydrogen and palladium-black to reduce a small amount of unsaturated material which was present. The product slowly crystallised, and after trituration with acetic acid yielded white crystals (4·2 g.), m. p. 151—154°. β-1-*Hydrindyl-α-naphthoic acid* (II) crystallised from benzene in colourless lustrous prisms, which dried to a powder, m. p. 155—156° (Found : C, 83·2; H, 5·6. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%).

Cholanthrene.—The finely powdered acid (II) (1 g.) was dissolved in ice-cold concentrated sulphuric acid (5 c.c.), and the solution kept at 0° for 2 hours. The yellow precipitate obtained by pouring it on ice was insoluble in sodium carbonate solution, and with boiling sodium hydroxide gave the typical orange-yellow colour with a green fluorescence characteristic of an anthranol. The compound was undoubtedly the anthrone (III) or its enolic tautomeride, but isolation in the pure state was not attempted. Reduction was effected by boiling 3N-sodium hydroxide (100 c.c.) and zinc dust (3 g.) in 4 hours. The suspended solid was then collected, and digested with hydrochloric acid to remove the excess of zinc. The residue was collected, and sublimed at 210—215°/0·2 mm. The pale yellow sublimate (0·8 g.) was recrystallised from benzene-alcohol, yielding pure cholanthrene, m. p. 168·5—170° (picrate, m. p. 167—168°).

Cholanthrene (0·3 g.) was oxidised with sodium dichromate in boiling acetic acid, and the acidic product extracted and recrystallised from xylene and then acetic acid. 1 : 2-*Benzanthraquinonyl-5-acetic acid* formed yellow leaflets which decomposed at 245—265° (Found : C, 74·9; H, 3·9. $C_{20}H_{12}O_4$ requires C, 75·9; H, 3·8%). Decarboxylation of this acid gave 5-methyl-1 : 2-benzanthraquinone (compare this vol., p. 670).

Condensation of 1-*Bromo-2-naphthylmagnesium Iodide with* α-*Hydrindone*.—1-Bromo-2-iodonaphthalene (Meldola, J., 1885, **47**, 523) (2·7 g.) and magnesium turnings (0·2 g.) were added to a Grignard solution prepared from ethyl bromide (0·6 c.c.), magnesium (0·2 g.), and ether (20 c.c.). After boiling for 3 hours, the cooled solution was treated with α-hydrindone (2·2 g.) in ether (10 c.c.). The product was isolated in the usual way, and distilled. The fraction, b. p. 210°/0·1 mm., formed an orange gum which crystallised from ligroin. Recrystallisation from alcohol gave slender yellow needles, m. p. 142—143° (Found : C, 88·3; H, 5·8. $C_{19}H_{14}O$ requires C, 88·4; H, 5·4%).

175. *A Volumetric Determination of the Atomic Weight of Terbium.*

By Joseph K. Marsh.

The present accepted value for the atomic weight of terbium (159·2) rests solely on Urbain's determination (*Compt. rend.*, 1906, 142, 957) of the ratio of the anhydrous sulphate to the octahydrate.

The preparation of pure terbium material by fractionation of the dimethylphosphate has already been described (Marsh, J., 1934, 1972). This material has now been used in determining the ratio $Tb_2O_3 : 3C_2O_3$ by ignition of the oxalate and by titration with standard permanganate. The value derived for the atomic weight is 158·9.

Preparation of Materials.—Nitric acid distilled from silver was redistilled from resistance glass, and the middle fraction taken; 10 ml. on evaporation gave no weighable residue. Terbium peroxide was dissolved in this acid, and the solution diluted to contain 1 g. in 50 ml. and $N/2$ concentration of free acid. Reagent oxalic acid was twice crystallised from dilute nitric acid; 5 g. on slow sublimation gave no weighable residue. A hot 10% oxalic acid solution was added slowly to the hot terbium nitrate solution, with vigorous stirring, till in slight excess. The reaction mixture was kept on the water-bath for several hours till the precipitate had become more granular. The bulk of the liquid was then decanted and treated with half its volume of 10% oxalic acid; on cooling, crystals of terbium oxalate up to 1 mm. long separated, but as these were troublesome to dissolve during the permanganate titration, they were kept apart. The oxalate was collected in a Jena-glass funnel, and washed back into a beaker three times. Finally, it was washed in the funnel with a little alcohol, spread on a clock glass, dried at 30°, and kept protected from dust but freely exposed to the air for 2 days with occasional mixing. It was then thoroughly mixed and stored in a stoppered bottle.

Density of Terbium Oxalate.—Two or three large crystals about 1 mm. long were selected, and a bromoform–chloroform mixture prepared in which they remained suspended. The density found was 2·60.

Density of Terbium Oxide.—About 3·8 g. were placed in a 5 ml. density bottle and covered with hot, air-free water. The bottle was then placed in a vacuum desiccator, and the water cautiously boiled under reduced pressure till all entangled air was extracted. The density thus found was 7·68.

Ignition of Terbium Oxalate.—This was done in transparent silica crucibles in an electric furnace. The crucibles were ground flat at the top and the lids were similarly ground so that when they were in place the crucibles were practically air-tight, and their contents protected from assimilation of carbon dioxide and moisture. Heating the oxalate from room temperature to dull red occupied 2 hours. Not much apparent change took place below 350°, but shrinkage and darkening then began, and the rate of heating was reduced. After a time, the temperature was quickly raised to 1000° and maintained for 5 hours. The crucible was wholly or largely uncovered, and the furnace not too tightly closed to allow of ready escape of carbon dioxide. The dark brown peroxide thus formed was next reduced in a stream of hydrogen in a circular iron box placed in the electric furnace. Reduction occurred at a dull red heat, but a temperature of 700—800° was employed for 1/4 hour. Cooling was hastened by quenching in water, and if the contents were white the crucible was quickly transferred to a desiccator, and weighed after 40—60 minutes. The results are tabulated below:

Oxalate, g.	0·8046	1·16364	1·33993	1·27706	1·14461
Oxide, g.	0·38337	0·55446	0·63838	0·60848	0·54333
Oxide, %	47·655	47·649	47·643	47·647	47·644
					Mean 47·648

Weighings throughout have been corrected to vacuum standard..

Determination of Oxalate Radical.—Sørensen's sodium oxalate (Riedel Haën A.-G.) was used to standardise $N/10$-potassium permanganate. An aqueous solution of 20 ml. of concentrated sulphuric acid and 1 g. of manganese sulphate per litre was boiled till air-free and then treated with potassium permanganate. 5 L. caused rapid decolorisation of a few drops, but later, disappearance of colour occurred only after several minutes, and finally a single drop caused a permanent tint distinctly visible in 5 l. but not in 250 ml. 250 Ml. of this solution were used in each titration to dissolve the oxalate. A 50 ml. burette with N.P.L. certificate of corrections was used. Small weighing vessels of about 1 ml. capacity were made from the bottoms of speci-

men tubes. These with their contents were dropped into the titration liquid, and standard practice followed.

The permanganate used for Expts. 1—4 was found to be $1·0105N/10$ (1·01040, 1·01041, 1·01047 in separate determinations), and that for Expts. 5—8 was $1·0084N/10$ (1·00863, 1·00782, 1·00876).

The atomic weight was calculated from the contents of oxide and of C_2O_3 by means of the

expression : atomic weight $= \left(\dfrac{\% \text{ oxide}}{\% \ C_2O_3} \times 108\right) - 24.$

Determination of Oxalate, and Atomic Weight.

No.	Terbium oxalate, g.	Titration, ml.	C_2O_3, %.	Atomic weight.	No	Terbium, oxalate, g.	Titration, ml.	C_2O_3, %.	Atomic weight.
1	0·34336	26·56	28·139	158·88	5	0·57361	44·48	28·140	158·81
2	0·32038	24·767	28·119	159·00	6	0·58153	45·08	28·141	158·86
3	0·32307	24·99	28·139	158·88	8	0·62028	48·11	28·157	158·76
4	0·56839	43·92	28·110	159·06				Mean	158·89±0·04

(No. 7 gave a value 158·66, which has been rejected.) The following atomic weights were used : Na = 22·997, C = 12·00. Should the value for carbon be raised to 12·01 the value for terbium would become 158·92, but the aim of this work has been to determine only the first place of decimals and the value 158·9 is obtained. This figure is in complete accord with the work of Aston (*Proc. Roy. Soc.*, 1934, *A*, **146**, 46), who finds terbium to have only the mass number 159. The packing fraction may be expected to reduce this by about 0·08. Hence, chemical and mass-spectroscopic methods both indicate a value 158·9 for the atomic weight of terbium.

Thanks are tendered to Prof. Soddy and Messrs. Brewer and Lambert for facilities provided.

THE OLD CHEMISTRY DEPARTMENT, THE MUSEUMS, OXFORD.

176. *A Simple Relation between Molecular Polarisation in Solution and the Dielectric Constant of the Solvent.*

By RAYMOND J. W. LE FÈVRE.

THE expression $_0P_1/_0P_2 = K(\varepsilon_2 + 2)/(\varepsilon_1 + 2)$, in which $_0P_1$ and $_0P_2$ are the orientation polarisations of a solute molecule in two media of dielectric constants ε_1 and ε_2 respectively, appears to be valid over a wide range of ε values. Three groups of examples of its applicability are given in the following tables : (*a*) for pairs of solutions, (*b*) for solutions, and the corresponding solutes in the vapour states, and (*c*) for solutions, and the (liquid) solutes in bulk.

(*a*) *Pairs of Solutions.*—The solvents are indicated under S_1 and S_2; except where otherwise stated by the authors to whom reference is made, $_0P_1$ and $_0P_2$ are in each case taken as the differences between the total polarisations extrapolated to infinite dilution and the molecular refractions for the Na_D line; T is the temperature at which both measurements were made; the appropriate references are listed on p. 775. The value of the constant K is seen to be about unity.

T.	S_1.	$_0P_1$.	ε_1.	S_2.	$_0P_2$.	ε_2.	K.
			Nitrobenzene.				
25°	C_6H_6 [1]	321·2	2·273	CCl_4	320·5	2·227	1·01
	$CHCl_3$ [1]	208·6	4·724	C_6H_6	321·2	2·273	1·02
25	cyclo-C_6H_{12} [1]	327·4	2·016	n-C_6H_{14} [1]	339·9	1·887	1·00
	CCl_4 [1]	320·5	2·228	$C_{10}H_{16}$ [1]	320·3	2·162	1·02
	CS_2 [1]	277·4	2·633	C_6H_6	321·2	2·273	0·94
	$CHCl_3$ [1]	208·6	4·724	CS_2	277·4	2·633	1·09
	,,	,,	,,	n-C_6H_{14}	339·9	1·887	1·06
	,,	,,	,,	cyclo-C_6H_{12}	327·4	2·016	1·07
20	CCl_4 [2]	340·2	2·236	n-C_6H_{14}	344·8	1·912	1·07
	C_6H_6 [2]	329	2·282	$C_{10}H_{16}$	350	2·16	0·97
	CS_2 [2]	294·5	2·640	n-C_6H_{14}	344·8	1·92	1·01
18·5	C_6H_5Cl [2]	169·6	5·82	C_6H_6	335	2·241	0·93

3 B

T.	S₁.	₀P₁.	ε₁.	S₂	₀P₂	ε₂	K.
				Chlorobenzene.			
20°	C_6H_6 [2]	50	2·28	CCl_4	50	2·23	1·01
	CS_2 [2]	44·5	2·64	C_2Cl_4	49	2·30	0·96
	CCl_4 [2]	50	2·23	$C_{10}H_{18}$	52	2·16	0·98
	$C_{10}H_{18}$ [2]	52	2·16	cyclo-C_6H_{12}	53	2·02	1·02
	cyclo-C_6H_{12} [2]	53	2·02	C_6H_{14}	55	1·91	0·99
18	C_6H_5Me [3]	55	2·347	C_6H_6	51·5	2·241	1·09
25	Dioxan [13]	50·1	2·306	cyclo-C_6H_{12}	53	2·02	1·01
				o-Dichlorobenzene.			
20	CS_2 [2]	95	2·64	C_6H_6	111·5	2·28	0·92
	C_6H_6 [2]	111·5	2·28	$C_{10}H_{18}$	106·5	2·16	1·08
	$C_{10}H_{18}$ [2]	106·5	2·16	n-C_6H_{14}	111	1·91	1·02
				Acetone.			
20	$C_{10}H_{18}$ [2]	158	2·16	n-C_6H_{14}	169	1·91	0·99
	C_2C_6 [2]	160	2·28	CCl_4	176	2·23	0·92
	CS_2 [2]	154	2·64	C_6H_6	160	2·28	1·04
18·5	$C_6H_5·NH_2$ [3]	118·4	7·23	$CHCl_3$	149·7	5·04	1·04
				Benzophenone.			
20	CS_2 [2]	174	2·64	C_6H_6	184	2·28	1·03
	C_6H_6 [2]	184	2·28	CCl_4	186	2·23	1·00
	CCl_4 [2]	186	2·23	$C_{10}H_{18}$	181	2·16	1·04
	$C_{10}H_{18}$ [2]	181	2·16	n-C_6H_{14}	185	1·91	1·04

It is to be noted that the relation now proposed satisfactorily includes the data for the polar solvents, chloroform, aniline, and chlorobenzene; the rule previously given by Jenkins [1] (*viz.*, total polarisation $\propto$ 1/dielectric constant of solvent) fails in this respect, as is seen from the following data :

Total polarisation of nitrobenzene in various solvents at 25°.

S₁.	Total P₁	ε₁	S₂	Total P₂.	ε₂.	P₁ε₁/P₂ε₂.
cyclo-C_6H_{12}	360	2·016	n-C_6H_{14}	372·5	1·887	1·03
CCl_4	353·1	2·228	$C_{10}H_{18}$	352·9	2·162	1·03
CS_2	310·0	2·633	C_6H_6	353·8	2·273	1·01
$CHCl_3$	341·2	4·722	CS_2	310	2·633	1·97
,,	,,	,,	C_6H_6	353·8	2·273	2·00
,,	,,	,,	n-C_6H_{14}	372·5	1·887	2·29

(b) *Solutions, and Solutes as Vapours.*—If ε₂ is put = 1, and ₀P₁ has the significance defined in section (a), then $_0P_1/_0P_2$ gives the ratio between the orientation polarisations in the dissolved (infinitely dilute) and in the gaseous state; K in this case is higher than unity :

T.	S₁	₀P₁	ε₁.	S₂	₀P₂	K.	T.	S₁.	₀P₁.	ε₁.	S₂	₀P₂.	K.
				Chlorobenzene							*Nitrobenzene.*		
20°	C_6H_6 [1]	50	2·28	Vac [5]	58·1	1·23	18·5°	C_6H_5Cl [1]	169·6	5·82	Vac.[4]	377·3	1·17
							25	C_6H_6 [1]	321·2	2·273	,,	373	1·22
			n-Propyl chloride				25	$CHCl_3$ [3]	208·6	4·724	,,	,,	1·25
20	n-C_6H_{14} [3]	84	1·91	Vac [7]	87·8	1·25					*Acetone.*		
	$C_{10}H_{18}$ [2]	82	2·16	,,	,,	1·29							
	CCl_4 [1]	80	2·23	,,	,,	1·28	20	n-C_6H_{14} [2]	169	1·91	Vac.[6]	175	1·26
	C_6H_6 [1]	77·5	2·28	,,	,,	1·26		$C_{10}H_{18}$ [2]	169	2·16	,,	,,	1·34
	C_2Cl_4 [1]	77	2·30	,,	,,	1·26		C_6H_6 [2]	160	2·28	,,	,,	1·30
	CS_2 [2]	68	2·64	,,	,,	1·20		CS_2 [2]	154	2·64	,,	,,	1·36

Müller's rule [10] [that $_0P_{soln.}/_0P_{gas} = 1 - k(\varepsilon - 1)^2$], when applied to the above data, is found to hold only for solvents of low dielectric constant (for which $k = 0·075 \pm 0·005$) ; it breaks down for chloroform ($k = 0·032$) and chlorobenzene ($k = 0·035$).

(c) *Solutions, and Solutes in Bulk.*—For a given substance, the expression relates measurements made on dilute solutions with those on the undissolved material; thus a liquid in bulk can be regarded as a solution of itself in itself, *i.e.*, in a solvent S₁ of dielectric constant ε₁. For most of the cases worked out, K lies between 1 and 2, an observation which suggests a simple method for the approximate determination of the dipole

moment of a liquid substance of known type : from the dielectric constant, density, molecular weight, and refractive index of the substance *in bulk*, the atomic plus orientation polarisation in, say, benzene can be calculated by the general equation as $_0P_1(\varepsilon_1 + 2)/4 \cdot 273K$; then at 25° μ will equal $0 \cdot 22[_0P_1(\varepsilon_1 + 2)/4 \cdot 273K]^{\frac{1}{2}}$ Debye units.

In the following table $_0P_1$ is the difference between the value of $[(\varepsilon_1 - 1)/(\varepsilon_1 + 2)]M/d$, and the molecular refraction for sodium light ; $_0P_2$ has the meaning used in Section (a).

T.	S_1.	$_0P_1$.	ε_1.	S_2.	$_0P_2$.	ε_2.	K.
20°	$Me \cdot NO_2$ [15]	37·25	39·4	C_6H_6 [17]	192·5	2·280	1·85
25	$Ph \cdot NO_2$ [8]	62·27	35·22	C_6H_6 [1]	321·2	2·273	1·69
,,	,,	,,	,,	CCl_4 [1]	320·5	2·227	1·71
,,	,,	,,	,,	$CHCl_3$ [1]	208·6	4·724	1·65
				C_6H_5Cl [8]	169·6	5·82	1·74
25	$o\text{-}C_6H_4Me \cdot NO_2$ [15]	68·7	20·07	C_6H_6 [13]	293	2·273	1·54
20	C_6H_5Cl [8]	31·99	5·82	C_6H_6 [2,8]	51·1	2·28	1·14
,,	,,	,,	,,	CCl_4 [2,8]	51·1	2·23	1·16
,,	,,	,,	,,	CS_2 [2,8]	45·6	2·64	1·18
,,	,,	,,	,,	$n\text{-}C_6H_{14}$ [2,8]	56·1	1·91	1·14
,,	,,	,,	,,	C_2Cl_4 [2,8]	49·1	2·30	1·18
	$COCl_2$ [15]	21·34	4·724	CCl_4 [14]	27·4	2·275	1·23
25	$COMe_2$ [8]	48·1	20·87	CCl_4	154	2·227	1·69
18	$COPhMe$ [15]	63·1	18·31	C_6H_6 [8]	187·5	2·241	1·61
25	$CHCl_3$ [8]	24·3	4·80	C_6H_6	26·5	2·273	1·46
				CCl_4	28·8	2·227	1·36
20	$C_6H_5 \cdot CO_2Me$ [11]	43	6·633	C_6H_6 [11]	67·9	2·280	1·28
20	$MeCN$ [15]	37·16	36·2	C_6H_6 [16]	251	2·280	1·32
25	$C_6H_5 \cdot NH_2$ [19]	28·81	6·677	C_6H_6 [11]	50·8	2·273	1·15
25	$C_6H_5 \cdot NHMe$ [19]	31·96	5·903	C_6H_6 [12]	57	2·273	1·04
25	$C_6H_5 \cdot NMe_2$ [19]	30·24	4·811	C_6H_6 [12]	53	2·273	0·91
25	C_5H_5N [19]	39·39	12·013	C_6H_6 [18]	109·4	2·273	1·18
25	C_5H_5N [19]	42·58	8·704	C_6H_6 [18]	99	2·273	1·08
25	$iso\text{-}C_6H_7N$ [19]	48·2	10·711	C_6H_6 [18]	132·2	2·273	1·08

Certain liquids, *e.g.*, water and alcohols, stand alone and yield constants which are considerably higher than the foregoing. Accurate dielectric-constant data are lacking, and we hope to make an experimental study of this group in the near future. The data for water and ethyl alcohol are given as examples :

25°	H_2O [8]	13·59	79·45	C_6H_6	60·2	2·273	4·30
,,	,,	,,	,,	Dioxan	78·2	2·306	3·29
				,,	75·3	,,	3·41
25	$EtOH$ [8]	40·5	24·69	CCl_4	61	2·227	4·19

Treatment in the same way of bulk-vapour state figures leads to similar results in the few cases where the available measurements permit a test to be made.

References used in the tables.

[1] Jenkins, *Nature*, 1934, **133**, 106. [2] Muller, *Physikal. Z* , 1933, **34**, 689. [3] Hassel and Uhl, *Z physikal. Chem.*, 1930, B, **8**, 187. [4] Calc. from results of Sugden and Groves, J., 1934, 1091. [5] Calc from Smyth and McAlpine, *J. Chem. Physics*, 1935, **3**, 55 [6] Zahn, *Physikal Z* , 1932, **33**, 686 [7] Sänger, *ibid.*, 1931, **32**, 20, *Helv. Phys. Acta*, 1930, **3**, 161. [8] Graffunder and Heymann, *Z. Physik*, 1931, **72**, 744. [9] Muller, *Physikal. Z.*, 1932, **33**, 731 [10] Muller, *Trans. Faraday Soc.*, 1934, **30**, 729 [11] Estermann, *Z. physikal. Chem.*, 1928, B, **1**, 134. [12] Williams, *Physikal Z.*, 1931, **32**, 27. [13] Schlundt and German, *J. Physical Chem.*, 1925, **29**, 353. [14] Le Fèvre, forthcoming paper. [15] Walden, *Z physikal. Chem* , 1910, **70**, 569. [16] Partington and Cowley, *Nature*, 1935, **135**, 474. [17] Partington and Hunter, J , 1933, 312. [18] Le Fèvre and Smith, J., 1932, 2810. [19] Present paper.

In the above tables $_0P$ has been taken, in nearly every case, as the difference between the total polarisation and the molecular refraction for sodium light, *i.e.*, with each example a different and probably inadequate allowance for the atomic polarisation contribution to the total polarisation has been made. The effects of an erroneously large orientation polarisation figure (increase of K, as, *e.g.*, in instance of nitromethane) will obviously be most marked, for arithmetical reasons, with the greater dielectric constant values [*i.e.*, Section (c)]. The indication, however, is that—applied to accurately corrected orientation polarisations—the constant is of the order unity.

The molecular polarisation $(= {_A}P + {_B}P + {_0}P)$ values shown by a substance in the liquid, dissolved, or gaseous state are now easily related. Recorded data show that a non-polar

solute ($_0P = 0$) has much the same molecular polarisation in all solvents: only polar solutes exhibit appreciable alterations. Therefore, since the distortion polarisation (= atomic and electronic polarisations) of a substance is usually practically independent of its state of aggregation, these differences are wholly referable to the orientation polarisation factor, the variations of which it is now shown can, in turn, be simply associated with the dielectric constant of the medium in which the solute molecules are dispersed.

Form and Physical Meaning of the Relation.—With the rather limited range of experimental data at present available, it is not possible to decide whether some similar relation of the type $_0P_1/_0P_2 - K(\epsilon_2 + n)/(\epsilon_1 + n)$ would not describe the facts better than the $\epsilon + 2$ expression used in this paper; *e.g.*, if $n = 3$, the first eight pairs of nitrobenzene solutions (p. 773) yield constants : 1·01, 0·95, 0·99, 1·01, 0·92, 1·03, 0·97, and 0·98 respectively.

For the time being, however, the $n = 2$ form is to be preferred, since it can be derived *a priori* from the not unreasonable assumption that the orientation polarisation of a solute molecule may, within limits, vary in some approximately direct manner with the space between the solvent molecules; this quantity, in 1 c.c. of a medium of dielectric constant ϵ, should be $1 - (\epsilon - 1)/(\epsilon + 2) = 3/(\epsilon + 2)$ c.c. (Clausius, "Mechanische Wärmetheorie," 2, 94), so that, generally, $_0P = 3k/(\epsilon + 2)$. Application to the case of a gas at low pressure shows, because $\epsilon_{\text{vac.}} = 1$, that the constant k is numerically the orientation polarisation in the vapour state. Clearly then, the ratio of the orientation polarisations developed by a given solute in two media of dielectric constants ϵ_1 and ϵ_2 is

$$_0P_1/_0P_2 = \frac{3k_1/(\epsilon_1 + 2)}{3k_2/(\epsilon_2 + 2)} = \frac{k_1}{k_2} \cdot \frac{\epsilon_2 + 2}{\epsilon_1 + 2} = K \frac{\epsilon_2 + 2}{\epsilon_1 + 2}$$

in which K should be exactly unity.

EXPERIMENTAL.

The dielectric constants and densities at 25° of the following pure liquids have been measured by the resonance and pyknometric methods employed previously (this vol., p. 480), and the total polarisations computed according to the Clausius–Mosotti relation in the usual way; these results, less the appropriate molecular refractions for sodium light, are tabulated in Section (c) above under ϵ_1 and $_0P_1$.

Aniline.—Purified by redistillation, b. p. 182—183°, and finally by freezing; $d_4^{25°}$ 1·01742, $\epsilon_{25°}$ 6·6773.

Methylaniline.—The commercial product was p-toluenesulphonated by the standard Schotten–Baumann process, and the derivative crystallised from dilute ethyl alcohol until of constant m. p.; hydrolysis, etc. (Ullmann, *Annalen*, 1903, 327, 110), afforded pure methylaniline, b. p. 193°/760 mm., $d_4^{25°}$ 0·98409, $\epsilon_{25°}$ 5·9032.

Dimethylaniline.—A commercial " pure " specimen was redistilled, b. p. 193°/760 mm., and twice frozen, m. p. 2—3°, $d_4^{25°}$ 0·95309, $\epsilon_{25°}$ 4·8114.

Quinoline.—Purified by distillation, b. p. 236—238°/761 mm., over lime, followed by freezing in a calcium chloride–ice mixture, m. p. − 20°, $d_4^{25°}$ 1·08979, $\epsilon_{25°}$ 8·7044.

isoQuinoline.—Purified by redistillation, b. p. 240°/762 mm., followed by freezing; m. p. 25°, $d_4^{25°}$ 1·09897, $\epsilon_{25°}$ 10·7108.

Pyridine.—A commercial " pure " specimen, after standing for two days over sodium hydroxide, was distilled; b. p. 114—115°/758 mm., $d_4^{25°}$ 0·97796, $\epsilon_{25°}$ 12·0132.

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177. *The Surface Tensions and Partial Vapour Pressures of Aqueous Aniline Solutions.*

By JAMES C. SPEAKMAN.

CALCULATIONS, based on an application of the Gibbs adsorption equation to the existing surface-tension data, of the minimum area occupied by an aniline molecule in the surface of its aqueous solution have led to an unexpectedly high result, *viz.*, 28·5 sq. Å. (*cf.* Rehbinder

and Taubmann, *Z. physikal. Chem.*, 1930, 147, 201; Kosakewitsch and Uschakowa, *ibid.*, 1931, 157, 168). In general, this value is higher than can be reconciled with the known dimensions of the aniline molecule, if it is assumed that a complete, unimolecular layer of orientated molecules is built up in the surface as the bulk concentration increases; and in particular, it is higher than the corresponding areas given by similar molecules according to the data collected by the last two authors (*e.g.*, *p*-toluidine 25·5, phenol 24 sq. Å.). It seemed possible that this anomaly might be due either to errors in the surface-tension data, or to failure of the implicit assumption that the concentrations and activities of aniline were identical. Several cases are known in which anomalies have arisen in the latter way. For instance, the minimum area calculated for a phenol molecule was also unaccountably high (36·5 sq. Å.) before the activity measurements were introduced by Goard and Rideal (J., 1925, 127, 1668). Again, with acetic acid solutions, when mole-fractions were used in the Gibbs equation, the minimum area occupied by each molecule in the surface was evaluated as about 43 sq. Å.; wholly suitable activity data do not seem to be available, but a rough application of those given by Lewis and Randall ("Thermodynamics," p. 290) reduces the calculated minimum area to approximately 30 sq. Å., which is more nearly in agreement with the areas given by the higher fatty acids.

For solutions of aniline, surface-tension measurements have been made by Worley (J., 1914, 105, 263) and by Seith (*Z. physikal. Chem.*, 1925, 117, 265), but, as the results of these workers do not agree, and as those of Seith do not cover the entire concentration range, these data have now been redetermined. Partial vapour pressures of aniline, which are assumed to be proportional to the activities, have also been measured.

EXPERIMENTAL.

Purification of Aniline.—The aniline was purified by shaking with dilute acid, washing with water, drying over solid potassium hydroxide, and two distillations under reduced pressure at about 60°. The product, which retained a slightly yellow tint, gave D_4^{20} 1·0216 and n_D^{20} 1·5860. Solutions were made in distilled water that had been boiled and cooled in a stream of nitrogen. They became somewhat coloured after several days, and over a period of some weeks their surface tensions appeared to diminish slightly (though this may have been due to the production of some substance which tended to contaminate the capillary tubes). For these reasons all measurements were made with freshly prepared solutions.

Surface Tensions.—Surface tensions were measured by a method previously described (J., 1933, 1449). Two sets of capillary tubes were used and gave concordant results within the limits of error ($\pm$ 0·2). All measurements were made at 20·0°, and the results are in Table I.

In calculating the surface tensions, an exact knowledge of the densities of the solutions was not needed, but they were determined in order that concentrations could, if desired, be converted into molalities or mole-fractions; the densities differed little from that of water, ranging from 0·9982 for the pure solvent to 1·0001 for the saturated solution. Owing to the difficulties which may arise in working with a saturated solution, its surface tension was not directly measured; by a short extrapolation this quantity was estimated to be 47·3 $\pm$ 0·2 dynes/cm.

The results obtained in this research differ widely from those of Worley, but agree approximately with those of Seith, who, however, worked at a rather lower temperature.

Partial Vapour Pressures.—Partial vapour pressures were determined by the modification of the gas saturation method, which depends on comparison of the unknown vapour pressure with that of pure water (cf., *e.g.*, Washburn and Heuse, *J. Amer. Chem. Soc.*, 1915, 37, 309;

TABLE I.

Surface tensions of aniline solutions.

Concn. (mols./l.).	γ (dynes/cm.).	Concn. (mols./l.).	γ (dynes/cm.).	Concn. (mols./l.).	γ (dynes/cm.).	Concn. (mols./l.).	γ (dynes/cm).
0·000	72·75	0·080	67·0	0·168	58·2	0·290	51·0
0·042	70·3	0·109	63·2	0·190	56·7	0·347	48·7
0·045	70·5	0·111	62·7	0·216	55·2	0·356	48·3
0·066	68·4	0·138	60·6	0·272	52·2		

Dobson and Masson, J., 1924, 125, 668). The gas used was nitrogen, stored in an aspirator over water, and passed thence through (1) a saturator containing water, (2) a first absorber

containing 98% sulphuric acid, (3) a pre-saturator and (4) a saturator, both containing the solution under investigation, (5) a second absorber, and (6) a guard-tube containing phosphoric oxide; (1), (3), and (4) were immersed in a thermostat at 20·0°. 3—4 Litres of gas were passed in each experiment at a rate of about 1 l./hr. The increase in weight of the first absorber represented the amount of water vapour carried over from the pure solvent, that of the second absorber the combined amounts of water and aniline vapours from the solution. The weight of the aniline alone (0·006—0·001 g. in these experiments) was found by diluting the sulphuric acid, running in excess of N/100-bromate–bromide solution, and estimating the excess iodometrically. From these data, the vapour pressure of pure water being taken as 17·53 mm., the partial vapour pressure of the aniline was calculated with the aid of the assumption that the vapour obeyed the simple gas equation; allowance was made for the fall of pressure through the apparatus as shown by appropriately placed manometers. The results, which could be reproduced to within 2%, are in Table II.

<div align="center">

TABLE II.

Partial vapour pressures of aniline.

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Concn. (mols./l).	Partial v.p. (mm).	Concn. (mols /l.).	Partial v.p. (mm.).	Concn. (mols./l.)	Partial v.p. (mm.).
0·066	{ 0·071 0·076	0·165	{ 0·164 0·167	0·312	0·295
0·080	0·085	0·190	0·195	0·356	{ 0·338 0·344
0·128	{ 0·136 0·139	0·221 0·256	0·220 0·256	0·385 (satd.; in presence of excess aniline)	{ 0·354 0·356 0·367

The experimental data were theoretically sufficient for calculating the partial vapour pressure of the water also, but this quantity differs so little from that of pure water that its variation lies below the limits of experimental error. However, it may be deduced thermodynamically that, for the range of concentrations over which the partial pressure of aniline obeys Henry's law (*i.e.*, up to about 0·2M), the partial pressure of water must obey Raoult's law; for more concentrated solutions, the change in the vapour pressure of the water can be obtained by a graphical integration of the Duhem–Margules equation, and it is concluded that the value for the saturated solution is 17·42 mm.

Solubility of Aniline in Water.—The concentration of the saturated solution at 20·0° was found to be 0·385M.

<div align="center">

DISCUSSION.

</div>

When Henry's law ceases to apply to the partial vapour pressures of aniline, it is no longer permissible to use concentrations instead of activities, and the adsorptions formerly calculated are incorrect. Values of the surface tension interpolated from a smooth curve were plotted against logarithms of corresponding similarly interpolated vapour pressures of aniline, and the adsorptions calculated in the usual way from the slope $-d\gamma/d\log p_a$ (cf. Table III). The slope increased with concentration, approaching a maximum value

<div align="center">

TABLE III.

Surface tensions, partial vapour pressures of aniline, and surface adsorptions of aniline (interpolated at round concentrations).

</div>

Concn. (mols./l)	0·000	0·050	0·100	0·150	0·200	0·250	0·300	0·350	0·385 (satd.)
γ (dynes/cm)	72·75	69·9	64·1	59·6	56·2	53·2,	50·6	48·5	47·3
Partial v.p. of aniline (mm.)	0·000	0·053	0·105	0·157	0·205	0·250	0·295	0·335	0·359
Adsorption (molecules/ cm.² × 10⁻¹⁴)	—	1·0	2·8	3·0	3·4	3·85	4·05	4·19	4·27

at saturation, which corresponded to a maximum adsorption of 4·27 ($\pm$ 0·05) $\times 10^{14}$ molecules per sq. cm. and to an area per molecule of 23·4 ($\pm$ 0·3) sq. Å.; this area agrees reasonably well with those found for similar molecules, and is consistent with the formation of a film composed entirely of aniline molecules at the surface. It is to be noted that this type of behaviour occurs with other partially soluble, surface-active solutes (*e.g.*, phenol)

and is likely to be general; a film of solute molecules is completed on the surface simultaneously with the bulk phase becoming saturated; as the proportion of solute is further increased, a second phase is laid down upon the foundation of this surface film, which then becomes an interfacial film.*

It has been customary to compare the minimum areas obtained in this way with those found by Adam for condensed films of the insoluble long-chain derivatives after extrapolation to zero compression. His value for aniline derivatives is 24 sq. Å. (" Physics and Chemistry of Surfaces," p. 50). It may, however, be doubted whether this comparison can be justified further than as an approximation. In the first place, the minimum areas obtained as in this paper do not correspond to zero compression; if the views of various authors (*e.g.*, Schofield and Rideal, *Proc. Roy. Soc.*, 1925, *A*, 109, 57) are accepted, the film must be regarded as under a compression of $\gamma_0 - \gamma$ dynes per cm., in the present instance equal to about 25 units. If the comparison were valid, therefore, it ought rather to be made with the area found by Adam for a like compression; actually this leads to a rather better agreement (*op. cit.*, p. 49), but the fact is not regarded as important. In the second place, it is generally held that the films given by soluble substances such as aniline are in a condition analogous to that of a gas above its critical point; if this is true, a comparison with the *condensed* film of an insoluble substance cannot be wholly satisfactory.

Corresponding values of F and FA/kT (cf. Schofield and Rideal, *loc. cit.*) were calculated from the present data. When plotted graphically, for values of F greater than 5, the points lay rather roughly on a straight line. The irregularity being disregarded (since the magnitude of FA/kT is very sensitive to slight errors in the data), the line may be represented by the equation $FA/kT = F . 17/kT + 0.4$, but the values of the constants are subject to considerable uncertainties.

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178. *Rhodium Hydroxopentammines.*

By BERTRAM E. DIXON.

IT has already been shown (J., 1934, 34) that iridium forms a series of hydroxopentammines, $[Ir(NH_3)_5(OH)]X_2$, which resemble the corresponding compounds of cobalt and chromium rather than those of platinum. It is now shown that rhodium forms a similar series of *hydroxopentamminorhodium* salts which bears a strong resemblance to that of iridium. These salts were prepared similarly to the iridium salts by the action of concentrated aqueous ammonia on the aquopentammines, which had been prepared by Jörgensen (*J. pr. Chem.*, 1886, 34, 394) by heating chloropentamminorhodium hydroxide solution, treating the cooled solution with silver hydroxide, and adding to the filtrate the appropriate acid.

The salts form well-defined, faintly yellow crystals, fairly easily soluble in water. Like the corresponding iridium salts, the rhodium hydroxopentammines are strongly alkaline to litmus, and liberate ammonia in the cold from ammonium salts. They are not basic aquo-salts, since (*a*) the *nitrate* is anhydrous, (*b*) there is no change in properties on heating to 100°, at which temperature an aquo-salt would be decomposed, and (*c*) their behaviour towards specific reagents is quite different from that of aquo-salts. The *bromide* and *sulphate* contain water of crystallisation which is completely expelled at 100°; that of $[Ir(NH_3)_5(OH)]Cl_2,H_2O$ requires a temperature of 135° for expulsion. The normal behaviour of the rhodium ammines in this respect confirms the conclusion previously reached, that the high temperature required for dehydrating $[Ir(NH_3)_5(OH)]Cl_2,H_2O$ was simply a case of the tenacity of water peculiar to some iridium ammines. There appears now no reason to doubt that the water in hydroxopentamminoiridium chloride is water of crystallisation.

* Although the bulk phases contain both components, the interfacial film will consist almost wholly of one component.

· The hydroxopentammines resemble the pentammine rather than the hexammine type in their behaviour towards specific ammine reagents.

The general stability of the hydroxopentammines depends, not only on the properties of the hydroxopentammine complex itself, but also on the character of the corresponding aquo-compound, which in many reactions is immediately formed as an intermediate compound. For instance, acetic anhydride leaves chromium hydroxopentammine (King, J., 1925, **127**, 2100) undecomposed, but acts on the much more stable rhodium hydroxopentammine with the formation of *acetato*-salt. When this factor is taken into consideration, it is seen that the rhodium hydroxopentammines, when they do occasionally differ slightly from their iridium counterparts (*e.g.*, in basicity, solubility, and colour), tend to approach in properties their other vertical neighbour, cobalt.

EXPERIMENTAL.

Titration values are expressed as percentage weight of hydrogen chloride required by the titrated substance.

Hydroxopentamminorhodium Bromide.—10 G. of aquopentamminorhodium bromide were placed in a flask fitted with a soda–lime guard-tube, and 120 ml. of freshly-distilled concentrated aqueous ammonia added from a dropping-funnel. Any substance remaining undissolved was filtered off as rapidly as possible, contact with the air being avoided, and the filtrate was returned to the flask. The flask was cooled, and 500 ml. of alcohol added gradually. The precipitate was filtered off, redissolved in 60 ml. of aqueous ammonia, and reprecipitated with alcohol. The crystals were collected, washed with alcohol and ether, and dried in a desiccator {Found : Rh, 26·8; N, 18·0; Br (total), 42·0; Br (free), 41·8; H_2O (loss at 100°), 4·8; titration, 9·6. [Rh(NH$_3$)$_5$(OH)]Br$_2$,H$_2$O requires Rh, 26·9; N, 18·3; Br (total), 41·7; Br (free), 41·7; H_2O, 4·7; titration, 9·5%}. The faintly yellow, microcrystalline *salt* does not change in weight on exposure to the air. It is fairly easily soluble in water, forming a solution which is strongly alkaline to litmus and can be sharply titrated with methyl-orange as indicator with one equivalent of acid. The water of crystallisation is expelled at 100°, and no change in colour, titre, or other properties is suffered on heating at 130° for several hours; under these conditions the aquo-salt changes to the brilliant yellow bromopentammine salt. All the bromine is precipitated in the cold by silver nitrate solution. A concentrated hydroxopentammine solution immediately evolves ammonia on the addition of solid ammonium chloride in the cold, and aquo-salt is formed. No precipitate is given when dilute solutions of silver nitrate and hydroxopentammine nitrate are mixed, but a fairly concentrated solution of silver nitrate added to the solid ammine gives a distinct darkening.

The reactions of the rhodium hydroxopentammines with typical ammine reagents are tabulated below; for comparison the reactions of acido- and aquo-salts (Jörgensen, *J. pr. Chem.*, 1883, **27**, 434; 1886, **34**, 394) are also given.

		Pentammines.	Hexammine.
Reagent.	Hydroxo-salt.	Acido-salt.	Aquo-salt.
Potassium ferricyanide, 5% soln.	After 30 mins., very small ppt. (yellowish-red prisms).	No ppt.	Immediate abundant ppt.
Sodium pyrophosphate, 5% soln.	No ppt. After 24 hrs., a few hexagonal plates.	No ppt.	Temporary ppt., dissolving in excess; permanent ppt. forms after 1 min.
Chloroplatinic acid soln.	Ppt. (yellow rhombs).	Ppt.	No ppt.
Sodium phosphate soln. and ammonium hydroxide.	Ppt. (white micro-crystals).	No ppt.	No ppt.
Sodium dithionate, 5% soln.	No ppt.	Ppt.	No ppt.

When carbon dioxide was passed through a cooled solution of the hydroxo-bromide, the resulting solution gave partial precipitates with potassium ferricyanide and sodium pyrophosphate solutions, indicating the presence of some aquo-salt. From the carbonated hydroxo-bromide solution, alcohol precipitated mostly unchanged hydroxo-bromide containing about 10% of carbonate.

Acetic acid reacted with hydroxo-salts to form aquo-salts; owing to its great solubility,

aquo-acetate could not be separated from the solution, but, on the addition of potassium bromide, alcohol, and ether, the aquo-bromide was precipitated.

Acetic anhydride (5 ml.) was rubbed with hydroxo-bromide (1 g.) in a mortar for 5 minutes, and the residue filtered off, washed with alcohol, redissolved in water, and reprecipitated with alcohol. The long, easily soluble, slightly yellow needles were *acetatopentamminorhodium bromide* {Found : Rh, 24·3; Br (free), 37·9; H_2O (at 100°), 4·3; titration, nil.

$$[Rh(NH_3)_5(O \cdot CO \cdot CH_3)]Br_2, H_2O$$
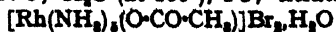
requires Rh, 24·2; Br (free), 37·6; H_2O, 4·2%; titration, nil}, and agreed in composition and properties with the salt formed by heating a solution of aquo-acetate with acetic acid.

From these tests, it is seen that carbonic acid is too weak to convert more than a small portion of the hydroxo-salt solution into aquo-salt, and shows no tendency to enter the complex. Acetic acid behaves as a mineral acid in forming the aquo-salt. With regard to the action of acetic anhydride on the bromide, it seems probable that some of the rather unstable aquo-salt is first formed, which is then decomposed to acetato-salt.

Hydroxopentamminorhodium Sulphate.—4 G. of aquopentamminorhodium sulphate were placed in the flask as before, and 50 ml. of cooled concentrated aqueous ammonia added. To the two immiscible layers so formed, 50 ml. of water were added, and the flask was shaken to dissolve the temporary precipitate. 200 Ml. of alcohol were added, and the slightly yellow crystals were collected and reprecipitated as in the preparation of the bromide {Found : Rh, 30·6; N, 20·6; SO_4 (total), 28·8; SO_4 (free), 28·6; H_2O (loss at 100°), 10·4; titration, 10·7. $[Rh(NH_3)_5(OH)]SO_4, 2H_2O$ requires Rh, 30·5; N, 20·8; SO_4 (total), 28·5; SO_4 (free), 28·5; H_2O, 10·7; titration, 10·8%}.

Hydroxopentamminorhodium Nitrate.—This *salt* was prepared from aquopentamminorhodium nitrate in a way similar to that described in the preparation of the bromide {Found : Rh, 31·0; N, 29·5; titration, 11·2. $[Rh(NH_3)_5(OH)](NO_3)_2$ requires Rh, 31·3; N, 29·8; titration, 11·1%}. The nearly colourless crystals were easily soluble in water and did not change in weight or in properties on heating at 100° for 8 hours. The nitrate was decomposed explosively on heating to higher temperatures, being in this respect more unstable than the corresponding iridium nitrate. In order to estimate the rhodium, a few drops of hydrochloric acid were added to the weighed salt in a porcelain crucible, and the contents of the crucible evaporated to dryness. This process was repeated, and the rhodium estimated by ignition in hydrogen as usual.

The author thanks Sir Robert Robertson for permission to publish this paper.

179. *Recent Progress in the Chemistry of the Terpenes.*[*]

By J. L. SIMONSEN.

THREE years ago the Society had the privilege of hearing Professor Ruzicka deliver the third Pedler Lecture (J., 1932, 1582). In giving an account of the life and work of Wallach the lecturer outlined much of the earlier work in terpene chemistry and it is the purpose of the present paper to attempt to survey briefly the more important advances which have been made during the past five years in the study of the isoprene (*iso*pentane) derivatives of essential oils. It is perhaps not generally recognised that, though the relationship of the terpenes to isoprene was noted and commented upon by both Wallach and Semmler, it was first used systematically by Ruzicka as a means of determining structure.

Of the simpler members of the terpene group, namely, those containing ten carbon atoms, our knowledge is now so complete in its main essentials that there is little to record. To the old controversy regarding the homogeneity of ·geraniol and related compounds, reference is made later (p. 784). We owe to Read and his collaborators important advances in the stereochemistry of the menthols and carvomenthols, and by an interesting series of reactions Houben and Pfankuch (*inter al., Annalen,* 1933, 501, 219; 507, 37) have converted *d*-camphor into *l*-camphor.

Two substances of great interest, a ketone and an aldehyde, have been described recently

and their constitutions determined. The ketone, jasmone, the odoriferous principle of oil of jasmine, has been shown independently by Treff and Werner (*Ber.*, 1933, 66, *B*, 1521) and by Ruzicka and Pfeiffer (*Helv. Chim. Acta*, 1933, 16, 1208) to be represented by (I). This ketone, which is not an isoprene derivative, contains a *cyclo*pentene ring and it is apparently the first occasion on which a substance containing this ring structure has been isolated from an essential oil. Its biochemical origin is obscure; it may possibly be formed from a 1 : 4-diketo-acid by intramolecular loss of water and elimination of carbon dioxide.

Of greater interest is the aldehyde, safranal, $C_{10}H_{14}O$, which Kuhn and Winterstein (*Ber.*, 1934, 67, *B*, 344) separated in the form of its glycoside, pikrocrocin, from saffron. This aldehyde has been shown to be represented by (II), and the glycoside by (III). Its

(I.) (II.) (III.) (R = glucose.)

association in nature with the polyene dicarboxylic acid, crocetin, naturally suggests that it is the parent of this substance or alternatively, and from analogy more probably, one of its degradation products (compare Mayer, " Chemie der organischen Farbstoffe," II, p. 47).

Safranal is obviously closely related to β-ionone, which Penfold and Philip (*J. Proc. Roy. Soc. W. Australia*, 1928, 14, 1) have shown to be present in the essential oil from *Boronia megastigma*, and to the two diketones, angustione (IV) and dehydroangustione (IVa), separated by Penfold (*J. Proc. Roy. Soc. N.S. Wales*, 1924, 57, 300) from the oil of *Back-*

(IV.) (IVa.) (V.)

housia angustifolia, their structure being determined later (Gibson, Penfold, and Simonsen, J., 1930, 1184; Cahn, Gibson, Penfold, and Simonsen, J., 1931, 286). The occurrence in nature of these simple ionone derivatives is of importance, since irone, to which Tiemann and Krüger erroneously assigned formula (V), has now been shown by Ruzicka and his collaborators (*Helv. Chim. Acta*, 1933, 16, 1143) to contain fourteen and not thirteen carbon atoms. The structure of this ketone, which possibly contains a *cyclo*heptane ring, has not been determined, but we cannot regret the mistake made by Tiemann and Krüger, since it led to the synthesis of α- and β-ionones, which have proved to be of such importance in the study of the structure of the carotinoids and of vitamin A.

Considerable advances have been made in the field of sesquiterpene chemistry. In the years immediately following the classical experiments on the dehydrogenation of cadinene and selinene to cadalene and eudalene respectively, Ruzicka and his collaborators determined the structure of the more readily accessible sesquiterpenes and sesquiterpene alcohols. Once the relationship to either cadalene or eudalene has been established, the elucidation of the constitution of a sesquiterpene affords comparatively little difficulty. With dicyclic terpenes having a bridged ring or with tricyclic members of the series, the difficulties are very much greater and our knowledge is still very limited.

Some progress has been made recently with one noteworthy group, the so-called caryophyllenes, the hydrocarbons occurring in oil of cloves. The investigations of Semmler and of Deussen had shown by the preparation of a number of crystalline derivatives that there were in the sesquiterpene fraction of this oil at least three hydrocarbons, designated α-,

β- and γ-caryophyllene respectively. The first of these is almost certainly identical with the hydrocarbon, humulene, first isolated by Chapman from hop oil. It probably differs completely in structure from the other two hydrocarbons, since it does not give a crystalline dihydrochloride or caryophyllenic alcohol on hydration. It was shown by Semmler in 1913 that caryophyllene (used here as a name for the mixture of hydrocarbons) on oxidation gave a liquid dibasic acid, caryophyllenic acid, which he suggested was methylnorpinic acid (VI). This acid has been shown (Evans, Ramage, and Simonsen, J., 1934, 1806; Ruzicka and Zimmermann, *Helv. Chim. Acta*, 1935, 18, 219) to be a mixture of two crystalline acids, norcaryophyllenic acid, $C_8H_{12}O_4$, and caryophyllenic acid, $C_9H_{14}O_4$. By the reactions indicated in the scheme given below, norcaryophyllenic acid has been shown to be d-cis-3 : 3-dimethyl*cyclo*butane-1 : 2-dicarboxylic acid (VII); and caryophyllenic acid must be (VIII) or (IX), since it can be degraded to norcaryophyllenic acid (Ramage and Simonsen, this vol., p. 532).

$$\begin{array}{ccccc}
\underset{\text{(VII)}}{\overset{\displaystyle Me_2C\text{—}CH\cdot CO_2H}{H_2C\text{—}CH\cdot CO_2H}} & \longrightarrow & \overset{\displaystyle Me_2C\text{—}C\cdot CO_2H}{H_2C\text{—}C\cdot CO_2H} & \longrightarrow & \overset{\displaystyle Me_2C\cdot CO_2H}{H_2C\cdot CO\cdot CO_2H} & \longrightarrow & \overset{\displaystyle Me_2C\cdot CO_2H}{H_2C\cdot CO_2H}
\end{array}$$

(VI) $Me_2C\underset{CH\cdot CO_2H}{\overset{CMe\cdot CO_2H}{<\quad>}}CH_2$

$\underset{\text{(VIII.)}}{\overset{\displaystyle Me_2C\text{—}CH\cdot CH_2\cdot CO_2H}{H_2C\text{—}CH\cdot CO_2H}}$

$\underset{\text{(IX)}}{\overset{\displaystyle Me_2C\text{—}CH\cdot CO_2H}{H_2C\text{—}CH\cdot CH_2\cdot CO_2H}}$

$H_2C\!:\!CH\cdot CHMe\ CH_2$

$Me_2C\text{—}C\quad CH_2$

$H_2C\text{—}CH\quad C\!:\!CH_2$

CH_2

(X.)
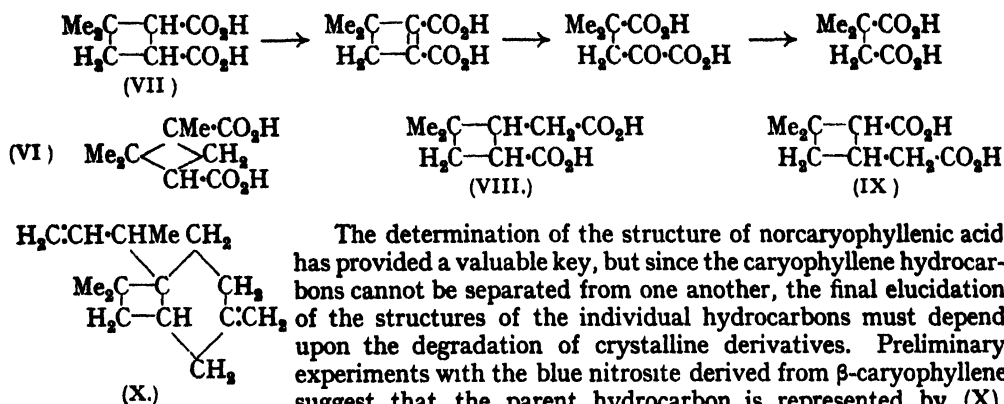
The determination of the structure of norcaryophyllenic acid has provided a valuable key, but since the caryophyllene hydrocarbons cannot be separated from one another, the final elucidation of the structures of the individual hydrocarbons must depend upon the degradation of crystalline derivatives. Preliminary experiments with the blue nitrosite derived from β-caryophyllene suggest that the parent hydrocarbon is represented by (X), according to which it would be derived from cadalene.

Attention has been directed recently to the chemistry of the santalols, since Penfold (*J. Proc. Roy. Soc. New South Wales*, 1928, 52, 60; 1932, 66, 240) has isolated from the wood oil of *Santalum lanceolatum* a new santalol containing three ethylenic linkages (Bradfield, Penfold, and Simonsen). As is well known, Semmler showed α-santalol to be the tricyclic alcohol (XI; R = OH), and β-santalol has now been found to be (XII; R = OH) (Bradfield, Penfold, and Simonsen, this vol., p. 309). This constitution was proved by the reactions outlined in the scheme :

$\overset{CMe}{\underset{\text{(XI.)}\ \text{(R = OH or Cl)}}{\begin{array}{l} HC\text{—}\!|\!\text{—}CH \\ \ \ |\ \ CMe|\cdot[CH_2]_2\cdot CH\!:\!CMe\cdot CH_2R \\ H_2C\ \ |\ \ CH_2 \\ \ \ \ CH \end{array}}}$ $\xrightarrow{NaCH(CO_2Et)_2}$ $\overset{CMe}{\begin{array}{l} HC\text{—}\!|\!\text{—}CH \\ \ \ |\ \ CMe|\cdot[CH_2]_2\cdot CH\!:\!CMe\cdot CH_2\cdot CH(CO_2H)_2 \\ H_2C\ \ |\ \ CH_2 \\ \ \ \ CH \end{array}}$

$\overset{CMe}{\underset{\text{(XII.)}\ \text{(R = OH or Cl.)}}{\begin{array}{l} HC\diagup\diagdown CH_2 \\ \|\ \ CMe|\cdot[CH_2]_2\cdot CH\!:\!CMe\cdot CH_2R \\ HC\ \ |\ \ CH_2 \\ \ \ \ CH \end{array}}}$ $\longrightarrow$ $\overset{CMe}{\begin{array}{l} H_2C\diagup\diagdown CH_2 \\ \ |\ \ CMe|\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CO_2H \\ H_2C\ \ |\ \ CH_2 \\ \ \ \ CH \end{array}}$
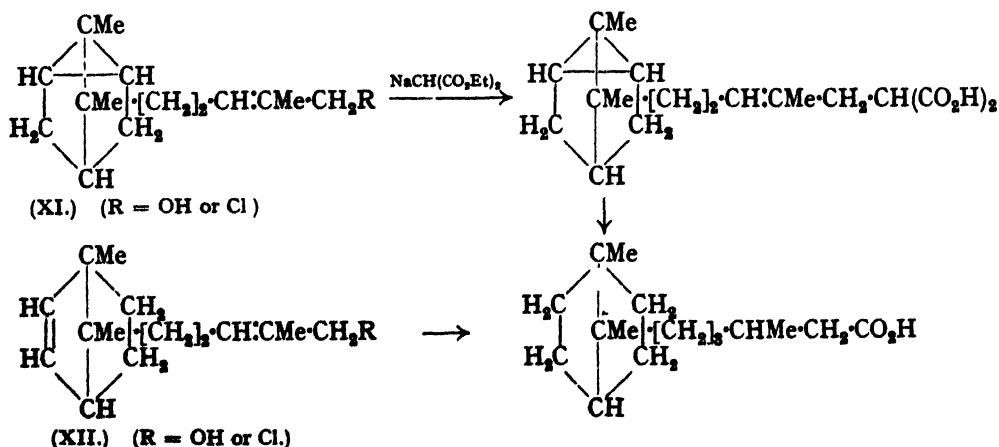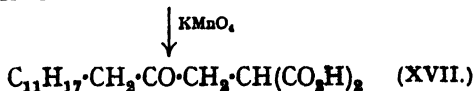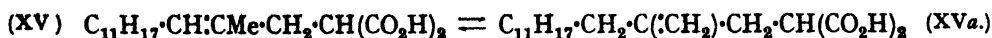
The contemporaneous experiments of Ruzicka and Thomann (*Helv. Chim. Acta*, 1935, 18,

355) suggest the presence of a third alcohol of the camphene type in sandalwood oil.[*] It is not without interest to note that, whereas α-santalol, as was pointed out by Ruzicka, is derived from eudalene, β-santalol may be regarded as a derivative of cadalene.

During the course of this investigation an observation of more general interest and importance was made. There has been much discussion as to the correct formulation of such simple terpene derivatives as geraniol, citral, etc., namely, as to whether they should be represented as having an *iso*propenyl or an *iso*propylidene group at the end of the chain. The majority of substances about which this discussion has ranged have been oils and the view most generally held has been that they were inseparable mixtures of substances containing these two groups. Kuhn and Roth (*Ber.*, 1932, **65**, *B*, 1258) have estimated quantitatively the acetone formed in the oxidation of a number of substances containing the *iso*propylidene group and have found it to vary from 60—90% of the theoretical value. They studied in particular the crystalline acid, dehydrogeranic acid (XIII or XIV), and here, in agreement with earlier observations (Cahn, Penfold, and Simonsen, J., 1931, 3134),

(XIII.) $Me_2C\!:\!CH\cdot CH\!:\!CH\cdot CH\!:\!CMe\cdot CO_2H$ $H_2C\!:\!CMe\cdot CH_2\cdot CH\!:\!CH\cdot CH\!:\!CMe\cdot CO_2H$ (XIV.)

both acetone and formaldehyde were obtained, the yield of acetone being only 60% of the theoretical value. Kuhn and Roth concluded that the acid was homogeneous and represented by (XIII), but the oxidation proceeded abnormally. A more satisfactory explanation has been provided by recent observations on the oxidation of α-santalylmalonic acid. When this acid, which is crystalline and readily purified, is oxidised with ozone, it yields practically quantitatively tri*cyclo*ekasantalal (or the corresponding acid) (XVI). On the other hand, in alkaline solution oxidation with potassium permanganate yields the keto-acid (XVII). The only adequate explanation appears to be that α-santalylmalonic acid exists in the tautomeric forms (XV) and (XVa).

(XV) $C_{11}H_{17}\cdot CH\!:\!CMe\cdot CH_2\cdot CH(CO_2H)_2 \rightleftharpoons C_{11}H_{17}\cdot CH_2\cdot C(\!:\!CH_2)\cdot CH_2\cdot CH(CO_2H)_2$ (XVa.)

$\downarrow O_3$ $\downarrow KMnO_4$

(XVI.) $C_{11}H_{17}\cdot CHO$ $C_{11}H_{17}\cdot CH_2\cdot CO\cdot CH_2\cdot CH(CO_2H)_2$ (XVII.)

These represent the *iso*propenyl and the *iso*propylidene form of the acid and tautomerism of this nature provides an adequate explanation of Kuhn and Roth's results with dehydrogeranic acid. It seems very probable that a similar tautomerism occurs also in the cases of geraniol, citral, etc.

The isolation of sesquiterpene ketones has opened up a new and interesting field of research. Although only a few members of this group have been described, there is little doubt that many of the sesquiterpene alcohols recorded in the literature will be found to be ketones. Two years ago the wood oil from *Eremophila Mitchelli* was shown to contain three closely related ketones, eremophilone (XVIII), hydroxyeremophilone (XIX), and


(XVIII.)   (XIX.)   (XX.)
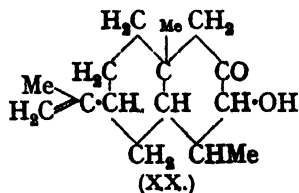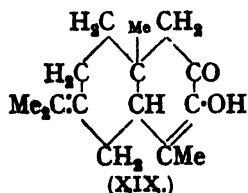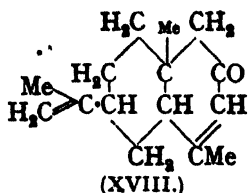
hydroxydihydroeremophilone (XX) (Bradfield, Penfold, and Simonsen, J., 1933, 2744). Their relationship to selinene and eudesmol was commented upon at the time. Shortly afterwards, St. Pfau and Plattner (*Helv. Chim. Acta*, 1934, **17**, 129) described two ketones, α-atlantone (XXI) and β-atlantone (XXII), occurring in cedar wood oil. Their presence

* The rotatory powers recorded by Ruzicka and Thomann for their α- and β-santalols indicate that their alcohols were impure. An alternative explanation to the one suggested above (occurrence of a third hydrocarbon) is that the conversion of α-santalylacetic acid into dihydro-β-santalylacetic acid is accompanied by a Wagner rearrangement.

in this oil had been overlooked previously, since α-atlantone is hydrolysed readily by alkali to 4-methyl-Δ¹-tetrahydroacetophenone (XXIII), which was erroneously considered to be a constituent of the oil.

(XXI.) (XXII.) (XXIII.)
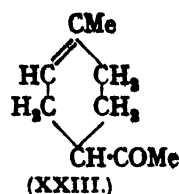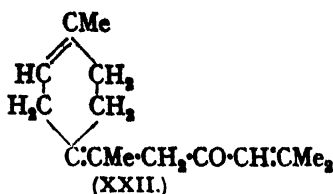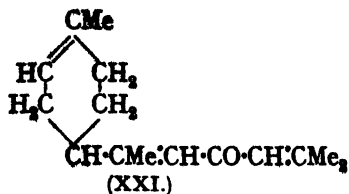
Closely related to these two ketones, but of an aromatic type, is the ketone turmerone present in admixture with sesquiterpenic ketones in the oil obtained from the tubers of *Curcuma longa*; this has been shown by Rupe, Clar, St. Pfau, and Plattner (*Helv. Chim. Acta*, 1934, 17, 372) to be represented by (XXIV). Turmerone on treatment with alkali yields curcumone (XXV), which has been prepared synthetically.

(XXIV.) (XXV.) (XXVI.)
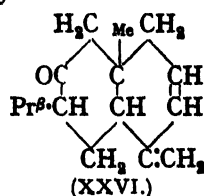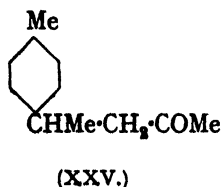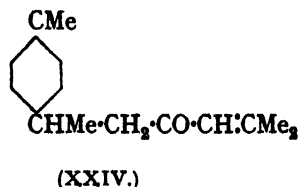
Recently B. Sanjiva Rao has isolated from the oil present in the tubers of *Cyperus rotundus* a sesquiterpene ketone, cyperone, which, like eremophilone, is a derivative of eudalene. This ketone has most probably the structure (XXVI) (Bradfield, Sanjiva Rao, and Simonsen).

Two outstanding problems in terpene chemistry remain to be solved. First, what is the mechanism of the formation of terpenes in plants and, secondly, what part do they play in the plant metabolism? With regard to the former problem, an admirable outline has been given by Robinson ("The Molecular Architecture of some Plant Products," IX Congreso Internacional de Quimica pura y aplicada, Madrid, 1934). It is simple on paper to derive any terpene from geraniol or α-pinene, but there seems to be little justification for such a procedure. It is not possible in the present state of our knowledge to go further than to regard, for example, α-pinene as the parent of myrtenal or verbenone. In the majority of theories the assumption is made that the more complex terpenes are built up from the simpler. Analogy would suggest that this assumption is incorrect. There seems to be little doubt that starch is the progenitor of the simpler saccharides, and the proteins of the alkaloids; it is more probable, therefore, that the simpler terpenes originate with the degradation of the polyterpenes. Our knowledge of the chemistry of these is still too limited for the elaboration of any definite scheme, but the occurrence of pikrocrocin in saffron supports the view advanced. Of the part the terpenes play in plant metabolism we are still ignorant, although some interesting investigations have been made recently in this connexion (Suchorukoda and Drushinina, *Sci. Mem. Univ. Saratov*, 1933, 10, No. 2, 81; Nilov, *Plant Inst. U.S.S.R.*, 1933, *A*, No. 7, 3).

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

180. *The Function of Sulphuric Acid in Nitration.*

By D. IVOR JAMES.

MOST of the work now reported formed part of a more extended investigation, conducted some years ago, to determine the optimal conditions for efficient trinitration of toluene, but Hetherington and Masson's results (J., 1933, 105) have suggested a new aspect of it. These authors found that, for the mononitration of nitrobenzene and nitrotoluene within the

limits of temperature and of molar concentration of sulphuric acid under which their experiments were conducted, " if there is at least enough sulphuric acid present to form the monohydrate H_2SO_4,H_2O with the water initially present *plus* the water formed chemically, the nitric acid is all available for this nitration," and that " temperature within our limits appears to play only a minor part in determining how far the reaction goes."

Trinitration, however, requires different temperatures and different concentrations of sulphuric acid from dinitration, and it by no means follows that the system represented by $H_2SO_4-HNO_3-H_2O$ has the same constituent composition under both conditions. It would seem that, other things being equal, it is the composition of this acid system that is the main factor in determining the course and end-point of the nitration. The results herein stated (Fig. 1), which concern the trinitration of toluene, show that up to a point, approximately represented by 95° and an excess of 4 mols. of H_2SO_4 beyond that required for monohydrate formation, the constituent components of the acid system, as indicated by the nitration products, remain the same, and the conclusions of Hetherington and Masson (*loc. cit.*) concerning the effect of sulphuric acid hold good. Within approximately these limits, at any given time the velocity of the reaction and, consequently, the percentage
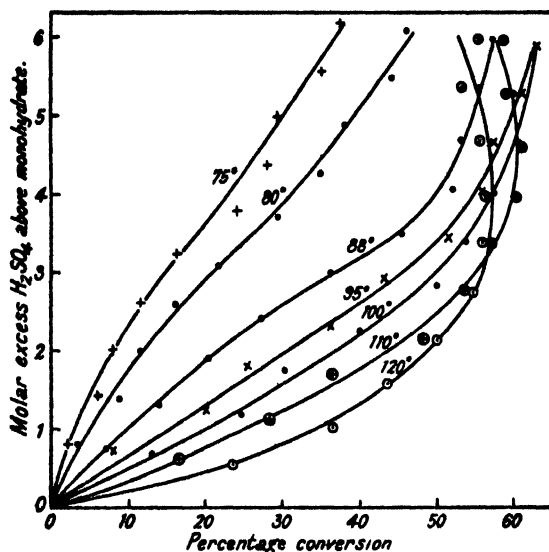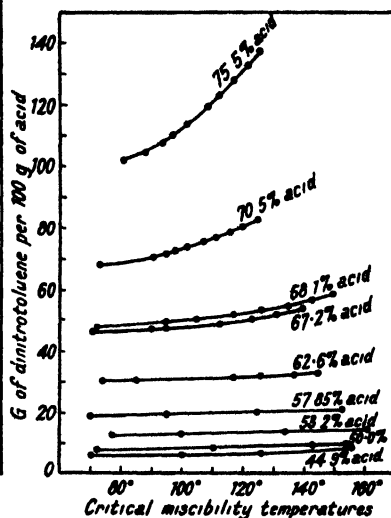

FIG. 1.   FIG. 2.

nitration, is a relatively simple function of the molar excess of sulphuric acid present, the action of the excess of acid being sufficiently explained by its effect on the miscibility of the dinitro-compound with the acid phase (Fig. 2).

Beyond these limits, the constituent composition of the nitrating acid appears to be different. Increase of temperature and of concentration of sulphuric acid progressively diminish the amount of nitric acid available for nitration as determined from the yield of nitro-compound. This effect is being investigated further, but quantitative balance-sheets constructed for a number of preliminary trinitrations show that the diminishing yields are not due to losses consequent on fuming, or on such side reactions as are customarily associated with nitration under these conditions. For instance, a typical experiment at 105°, in which the molar concentrations of the original components were represented by the ratios D.N.T. : HNO_3 : H_2O : $H_2SO_4 = 1\cdot0 : 1\cdot83 : 3\cdot60 : 8\cdot0$, revealed that, when after 5 hours the reaction had come to a virtual standstill, $9\cdot25\%$ of the dinitrotoluene remained unchanged although the spent acid contained $30\cdot0\%$ of the original nitric acid.

EXPERIMENTAL.

(1) 50 G. of pure 2 : 4-dinitrotoluene with 200 g. of sulphuric acid of the required concentration, in long-necked flasks loosely closed with glass wool, immersed in a large bath, were

nitrated with 13·5 c.c. (30 g.) of 96% HNO_3, the latter being added slowly in successive quantities of 3·7, 5·4, and 5·4 c.c. and the whole operation occupying 25 minutes. The flasks then remained in the bath for a further 20 minutes, being thoroughly agitated at 5-minute intervals. The products were poured into 2 l. of cold water, kept over-night, filtered off, washed thoroughly with 2 l. of running water at 95° under standardised conditions, dried at 110° for 5 hours, and their specific gravities determined in a 10-c.c. pyknometer after being kept at 90° for 15 minutes. Their composition was determined by comparison with a large-scale specific-gravity curve constructed from synthetic mixtures of pure 2 : 4-dinitro- and 2 : 4 : 6-trinitro-toluene at 90°. The isomeric trinitrotoluenes do not differ materially in specific gravity; consequently, their presence does not vitiate this determination.

A large-scale setting-point curve of these synthetic mixtures was also constructed for comparison; it shows a well-marked compound of approximately 3 mols. dinitrotoluene with 2 mols. trinitrotoluene of f. p. 45·9°, with eutectics of either constituent of f. p.'s 45·3° and 45·4° containing 37·0% and 47·5% respectively of trinitrotoluene. Guia (*Ber.*, 1914, **47**, 1718) found indications of such a compound on the m.-p. curve of these two substances, but the maximum on the curve between the two eutectics, recorded as 44·55° and 45·1° respectively, was too small to be determined. The specific-gravity curve shows a maximum deviation of 0·7% from the normal in the portion corresponding approximately to that of compound formation as indicated on the f.-p. curve.

The loss due to the method of isolation was small, not exceeding 2% of the original material.

Nitrations of 2 : 4-dinitrotoluene. (Initial molar proportions of the nitration mixture were D.N.T. : HNO_3 : H_2O : H_2SO_4 = 1·195 : 1·0 : x : y.)

Mols.			Temp.	75°.	80°.	88°.	95°.	100°.	110°.	120°.
x.	y.	Excess H_2SO_4.					Nitration, %.			
7·8	8·63	0·83		2·2	3·5	7·5	8·0	13·2	16·4	23·6
7·25	8·74	1·49		6·0	8·8	14·0	20·0	24·8	28·4	36·4
6·71	8·84	2·13		8·0	11·4	20·4	26·0	30·2	36·8	43·6
6·18	8·94	2·76		11·6	16·0	27·2	36·4	40·0	48·4	50·0
5·61	9·04	3·43		16·0	21·6	36·4	43·0	50·0	53·6	54·0
5·07	9·14	4·07		24·2	29·6	45·6	51·6	53·6	56·4	55·8
4·52	9·24	4·72		28·0	34·8	52·2	56·2	57·2	60·0	56·4
3·98	9·34	5·36		29·2	38·0	53·2	57·2	61·2	60·8	55·3
3·43	9·44	6·01		34·8	44·0	55·6	61·0	58·6	58·8	53·0
2·88	9·54	6·66		37·2	46·0	57·2	62·8	62·8	58·4	55·3

The import of these figures is clearly shown by plotting curves for percentage nitration against the molar excess of sulphuric acid beyond that required for monohydrate formation, adjustment having been made for the water formed by the nitration reaction (Fig. 1).

(2) The miscibility curves for the system D.N.T.–H_2SO_4–H_2O (Fig. 2) were constructed from the critical miscibility temperatures determined for a large number of synthetic mixtures of known composition. The method is accurate and rapid; the end-points are sharply defined and are the same whether observed on heating or on cooling. Concentrations of acid are expressed in molar percentages.

SUMMARY.

The conclusions of Hetherington and Masson (J., 1933, 105) concerning the effect of sulphuric acid on the mononitration of nitrobenzene and nitrotoluene are extended to the nitration of 2 : 4-dinitrotoluene. Up to a point, approximately represented by 95° and an excess of 4 mols. sulphuric acid beyond that required to form the monohydrate H_2SO_4,H_2O, the action of the excess of sulphuric acid is sufficiently explained by its promoting the miscibility of the components. Beyond this point, increase of temperature and increase of sulphuric acid concentration progressively diminish the amount of nitric acid available for nitration, as indicated by the yield of trinitro-compound. The investigation is being continued.

Fifth Report of the Committee on Atomic Weights of the International Union of Chemistry.

By G. P. BAXTER (Chairman), O. HÖNIGSCHMID, P. LEBEAU, and R. J. MEYER.

DURING the year the Committee has suffered an irreparable loss in the death of Mme. P. Curie, Professeur à la Faculté des Sciences de l'Université de Paris.

The following report of the Committee covers the twelve-month period, September 30, 1933, to September 30, 1934.*

Only one change has been made in the table of atomic weights, from 93·3 to 92·91 in the case of columbium (niobium).

CARBON.—Batuecas (*J. Chim. Phys.*, 1934, 31, 165) has determined the density of propylene at 0° and several pressures. Propylene was prepared by three methods : (1) action of phosphorus pentoxide on *n*-propyl alcohol, (2) catalytic dehydration of *iso*propyl alcohol by aluminium phosphate at 250—300°, (3) catalytic dehydration of propyl alcohol by active aluminium oxide at 270—300°. Chemical purification was followed by fractional distillation. Since the first method yielded a product difficult to purify, density determinations were made only with gas prepared by the second and third methods.

Values in the following table are calculated to 760 mm. ($g = 980·616$).

Density of propylene.

1 Atmosphere.

Method of preparation.	Globe G 1007·55 ml.	Globe N-3 772·58 ml.	Average.	Method of preparation.	Globe G 1007·55 ml	Globe N-3 772·58 ml.	Average.
2	1·9140	1·9148	1·9144	3	1·9154	1·9149	1·9152
	1·9147	1·9147	1·9147		1·9156	1·9151	1·9153
	1·9148	1·9158	1·9153		1·9144	1·9153	1·9149
	1·9145	1·9140	1·9147		1·9145	1·9147	1·9146
	1·9156		1·9156	Average	1·9149	1·9151	1·9150
	1·9142	1·9146	1·9144	Average of all	1·9148	1·9150	1·9149
Average	1·9146	1·9150	1·9148				

2/3 Atmosphere.

				1/2 Atmosphere.			
2	1·9003	1·9021	1·9012	2	1·8955	1·8959	1·8957
	1·9031	1·9031	1·9031		1·8961		1·8961
	1·9016	1·9030	1·9023	Average	1·8958	1·8959	1·8958
Average	1·9017	1·9027	1·9022	3	1·8954	1·8955	1·8955
3	1·9027	1·9011	1·9019		1·8963	1·8946	1·8955
	1·9023	1·9017	1·9020	Average	1·8959	1·8951	1·8955
Average	1·9025	1·9014	1·9020	Average of all	1·8958	1·8953	1·8956
Average of all	1·9020	1·9022	1·9021				

On the assumption that the change of PV with P is a linear one the following values are calculated :

$$1 + \lambda = 1·0204$$
$$C_3H_6 = 42·062$$
$$C = 12·005$$

CARBON AND NITROGEN.—Moles and Salazar (*Anales Soc. españ. Fís. Quím.*, 1934, 32, 954) have redetermined the densities of oxygen, carbon monoxide, and nitrogen, using the same (improved) apparatus for all three gases.

Oxygen was prepared by pyrolysis of (*a*) potassium permanganate and (*b*) potassium and sodium chlorates with manganese dioxide. Chemical purification was followed by fractional distillation.

Carbon monoxide was prepared (*a*) from potassium ferrocyanide and sulphuric acid

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* Authors of papers bearing on the subject are requested to send copies to each of the four members of the Committee at the earliest possible moment.

Prof. G. P. Baxter, Coolidge Laboratory, Harvard University, Cambridge, Mass., U.S A.; Prof. O. Hönigschmid, Sofienstrasse 9/2, Munich, Germany; Prof. P. Lebeau, Faculté de Pharmacie, 4, Avenue de l'Observatoire, Paris (6e), France; Prof. R. J. Meyer, Landshuterstrasse 11–12, W 30, Germany.

and (*b*) from formic acid and concentrated sulphuric acid. Chemical and physical purification followed.

Nitrogen, obtained from sodium nitrite and ammonium sulphate, was subjected to chemical purification.

The Density of Oxygen.

	760 mm.				380 mm.		
Method.	Globe G. 987·59 ml.	Globe N. 992·04 ml.	Average.	Method.	Globe G. 987·59 ml.	Globe N. 992·04 ml.	Average.
	1·42895	1·42899	1·42897	a	1·42832	·42827	1·42829
a	1·42892	1·42897	1·42894	a	1·42826	1·42835	1·42830
a	1·42903	1·42887	1·42895	a	1·42836	1·42831	1·42833
a	1·42896	1·42894	1·42895	a	1 42830	1·42841	1·42835
a	1·42893	1·42897	1·42895	a	1·42830	1·42835	1·42832
b	1·42897	1·42894	1·42895	b	1·42820	1·42833	1·42826
b	1·42897	1·42894	1·42895	b	1·42832	1·42829	1·42830
Average	1·42896	1·42895	1·42895	Average	1·42829	1·42833	1·42831

The Density of Carbon Monoxide.

	760 mm.				380 mm.		
Method.	Globe G.	Globe N.	Average.	Method.	Globe G.	Globe N.	Average.
a	1·24998	1·25000	1·24999	a	1·24978	1·24977	1·24977
a	1·25012	1·25001	1·25006	a	1·24970	1·24975	1·24972
a	1·24999	1·25001	1·25000	a	1·24978	1·24979	1·24978
	1·25000	1·24998	1·24999	a	1·24977	·24977	1·24976
b	1·25001	1·25001	1·25001	a	1·24978	·24971	1·24974
b	1·24998	1·25001	1·24999	a	1·24982	·24975	1·24978 .
b	1·25003	1·24998	1·25000	b	1·24974	·24970	1·24972
b	1·25002	1·25000	1·25001	b	1·24976	·21973	1·24974
Average	1·25002	1·25000	1·25001	b	1·24974	·24975	1·24974
				Average	1·24976	1·24975	1·24975

The Density of Nitrogen.

	760 mm.	
Globe G.	Globe N.	Average.
1·25049	1·25048	1·25049

	380 mm.	
1·25020	1·25023	1·25022

From these data are calculated the following values :

	Limiting density.	1 + λ.	Molecular weight.
Oxygen	1·42767	1·00090	
Carbon monoxide	1·24950	1·00040	28·006 (5)
Nitrogen	1·24995	1·00043	28·0165

The atomic weights of carbon and nitrogen, respectively, are thus found to be 12·006 (5) and 14·0083.

NITROGEN.—Moles and Sancho (*Anales Soc. españ. Fís. Quím.*, 1934, **88**, 931) dispute the claim of Dietrichson, Bircher, and O'Brien that very dry glass surfaces adsorb little or no ammonia, and attempt to correct the results of these authors and those of Dietrichson, Orleman, and Rubin on the density of ammonia by using the adsorption data of Moles and Crespi, and Crespi and Aleixandre.

They have also redetermined the density of ammonia at 0° and at 1 atmosphere and ½ atmosphere, using a volumeter method, in which the weight of ammonia is found by the gain in weight of a receptacle containing sulphuric acid.

Synthetic ammonia was dried with potassium hydroxide and barium oxide, and was fractionally distilled from liquid sodium–potassium amalgam.

Improved apparatus was employed. The barometer with its reservoir was maintained at 0° so that no temperature correction was necessary. The volumes of the globes were 5566·52 (G) and 2378·59 (P) ml. Corrections for the compressibility of ammonia were therefore made, as well as for adsorption on the basis of the work of Moles and Crespi.

3 F

Pressure.	Globe G.	Globe P.	Globes G + P.
1 Atmosphere	0·77143	0·77145	
	0·77131	0·77150	
	0·77152	0·77153	
	0·77137	0·77150	
Average	0·77141	0·77144	
		Average of all 0·77143*	
1/2 Atmosphere	0·76558	0·76558	0·76572
			0·76572
			0·76540
			0·76570
Average	0·76558	0·76558	0·76564
		Average of all	0·76562

* Incorrectly calculated.

The limiting density of ammonia is calculated on the assumption, which Moles and Sancho prefer, that the compressibility is a linear function of the pressure. The normal molal volume is assumed to be 22·4142 litres. The results on this basis are :

Limiting density	0·75981
Mol. wt. NH$_3$	17·0305
At. wt. N	14·007

The authors find 14·008 for nitrogen, but this value involves two arithmetical errors, one in the average density at one atmosphere and one in calculating the molecular weight of ammonia.

SODIUM.—Johnson (*J. Phys. Chem.*, 1933, **37**, 923) has redetermined the ratio of sodium chloride to silver. Sodium chloride was very carefully purified by precipitation with hydrogen chloride and crystallisation. During the last crystallisation it was divided into five fractions. The sodium chloride was fused in a weighed platinum crucible contained in an electrically heated quartz muffle and weighed. The fusion atmosphere in most cases was air, but in analyses 3 and 4 nitrogen was used, and in analysis 6 it was hydrogen chloride and nitrogen. An $N/5$-solution of the sodium chloride was then precipitated with an $N/5$-solution of a very nearly equivalent quantity of the purest silver and the end-point of the comparison was found at 0° with a nephelometer by the " standard solution " method recently developed by Johnson, and also in some cases potentiometrically. In half the analyses the silver solution was added to the chloride, in half the reverse method of precipitation was employed. Finally the silver chloride was collected, dried at 300°, and weighed. Dissolved silver chloride was estimated nephelometrically. Loss in weight of the silver chloride on fusion was not determined. Weights are corrected to vacuum.

The Atomic Weight of Sodium.

Fraction of NaCl.	Wt. of NaCl.	Wt. of Ag.	Ratio NaCl : Ag.	At. wt. Na.	Wt. of AgCl.	Ratio NaCl : AgCl.	At. wt. Na.
1	5·48994	10·13246	0·541817	22·994	13·46165	(0·407821)	(22·999)
1	5·43976	10·03981	0·541819	22·994	13·33993	0·407780	22·993
2	5·48976	10·13223	0·541812	22·994	13·46231	0·407787	22·994
2	5·47090	10·09724	0·541821	22·995	13·41552	0·407804	22·996
3	5·42144	10·00502	(0·541872)	(23·000)	13·29327	(0·407833)	(23·001)
3	5·4360	10·0340	(0·54176)	(22·988)	13·3307	(0·407780)	(22·993)
4.	5·59192	10·32064	0·541819	22·994	13·71263	0·407793	22·995
4	5·43087	10·02352	0·541813	22·994	13·31763	0·407796	22·995
5	5·51668	10·18218	(0·541798)	(22·992)	13·52883	(0·407772)	(22·992)
5	5·42755	10·01776	(0·541792)	(22·992)	13·31017	(0·407775)	(22·992)
		Average	0·541817	22·994		0·40779	22·994

The fifth analysis was rejected on the basis of disagreement, the sixth analysis on the basis of acidity of the sodium chloride, the ninth and tenth on the basis of impurity in the sodium chloride, and the first analysis for silver chloride on the basis of a known uncertainty.

The final result for sodium is 0·003 lower than the International value (22·997).

CALCIUM.—Smith and Tait (*Proc. Roy. Soc. Edinburgh*, 1934, **54**, 88) have compared calcium extracted from geologically old, potassium rich, calcium poor minerals with common calcium. Pegmatites from Portsoy, Banffshire, Scotland, and Rhiconich, Sutherlandshire, Scotland, were extracted with hydrochloric acid. About 30% of the original calcium was thus obtained. The purification consisted in five precipitations as oxalate, conversion into nitrate through the oxide, electrolysis of the nitrate solution, five crystallisations of the

nitrate, three precipitations as carbonate, conversion into chloride through the oxide, and one crystallisation as chloride (A). In each case a second sample was similarly prepared from the mother-liquors of the third nitrate crystallisation (B). For comparison two preparations were made in a similar way from marine shells from Fifeshire, Scotland, and coral limestone from Bermuda.

The calcium chloride was prepared for weighing by preliminary dehydration in a vacuum at low temperature and finally fusion in an atmosphere of nitrogen and hydrogen chloride in a bottling apparatus. After solution of the weighed salt a correction was determined for deviation from neutrality and then the solution was compared with pure silver in the usual way.

The Atomic Weight of Calcium.

Sample.	Wt. of CaCl$_2$.	Wt. of Ag.	Ratio CaCl$_2$: 2Ag.	At. wt. Ca.	Sample.	Wt. of CaCl$_2$.	Wt. of Ag.	Ratio CaCl$_2$: 2Ag.	At. wt. Ca.
Coral A	1·77727	3·45491	0·514419	40·077	Marine Shells A	2·02793	3·94230	0·514403	40·074
A	1·82493	3·54743	0·514437	40·081	A	2·09760	4·07770	0·514408	40·075
A	1·81606	3·53030	0·514421	40·077	B	2·23959	4·35360	0·514412	40·076
A	1·74543	3·39311	0·514404	40·074	A	2·18660	4·25062	0·514419	40·077
A	1·75771	3·41695	0·514409	40·075	B	2·13950	4·15897	0·514430	40·079
					B	2·04200	3·96947	0·514426	40·079
		Average	0·514418	40·077			Average	0·514416	40·076

Sample.	Wt. of CaCl$_2$.	Wt. of Ag.	Ratio CaCl$_2$: 2Ag.	At. wt. Ca.	Sample.	Wt. of CaCl$_2$.	Wt. of Ag.	Ratio CaCl$_2$: 2Ag.	At. wt Ca.
Portsoy B	1·70015	3·30465	0·514472	40·088	Rhiconich B	1·94278	3·77612	0·514491	40·093
B	1·78487	3·46928	0·514479	40·090	B	1·98782	3·86364	0·514494	40·093
A	1·74779	3·39721	0·514478	40·090	A	1·88677	3·66715	0·514505	40·096
A	1·69538	3·29562	0·514434	40·080 *	B	1·96884	3·82687	0·514478	40·090
B	1·87366	3·64188	0·514476	40·089	B	2·19803	4·27222	0·514494	40·093
B	2·07253	4·02853	0·514463	40·087	A	2·17033	4·21850	0·514479	40·090
		Average	0·514468	40·087			Average	0·514490	40·092

* Incorrectly calculated in the original paper.

The atomic weight found for common calcium (40·076) is not far from that found by Richards and Hönigschmid (40·074), but is lower than that found by Hönigschmid and Kempter (40·084). Some uncertainty exists as to the vacuum corrections for calcium chloride and silver applied by Smith and Tait, who took into consideration the densities of both the brass and the aluminium weights. If this was not done also in the standardisation of the weights, the vacuum corrections as applied are incorrect. The possible error in the atomic weight of calcium would vary with the proportion of fractional weights employed, and in the experiments of Smith and Tait may amount to from + 0·008 to − 0·007.

The differences in the atomic weight of calcium from the different sources are used to calculate the half life of ^{41}K (See Fourth Report of this Committee).

KRYPTON.—Heuse and Otto (*Physik. Z.*, 1934, **35**, 57) have redetermined the density of krypton. The gas was carefully purified first with hot calcium, then by fractional distillation. The coefficient of compressibility was found at 0° to be − 0·00279 and the temperature coefficient 0·0036609 + 358 × 10^{-7} p (metres). With a 267·53-ml. globe the following results were obtained, using the density of oxygen 1·42900 and the compressibility coefficient − 0·00094.

The Density of Krypton.

Weight.	Pressure.	Temperature.	Density.	At. wt. Kr.
0·83479	681·84	20·60°	3·7432	83·668
0·85258	684·27	15·50	3·7428	83·659
0·84484	681·32	16·87	3·7427	83·657
0·88107	715·13	19·11	3·7433	83·670
		Average	3·743	83·66

COLUMBIUM (NIOBIUM).—Hönigschmid and Wintersberger (*Z. anorg. Chem.*, 1934, **219**, 161) have determined the ratio of columbium pentachloride to silver. Potassium columbium oxyfluoride was fractionally crystallised from hydrochloric acid solution with rejection of the most soluble and the least soluble (containing tantalum) fractions, until the head fraction gave no evidence of tantalum upon X-ray analysis (Prandtl and von Hevesy). The product was converted into sodium columbate and residual iron was removed with ammonium sulphide. Next columbic acid was precipitated with sulphurous acid, washed,

and ignited. Further extraction with hydrochloric acid and water followed. This material still contained titanium and a trace of zirconium (Sample I).

Purified columbic acid, prepared by Fetkenheuer but still containing 0·1% of tantalum, was converted into potassium columbic oxyfluoride, and this substance was fractionally crystallised until free from tantalum. Zirconium was removed by fusion with potassium carbonate and extraction, and iron was removed as sulphide. Columbium was then precipitated with salicylic acid to eliminate titanium, and the precipitate was ignited to oxide (Sample II).

A portion of Sample I was freed from zirconium as in the case of Sample II (Sample III).

Solutions obtained in the course of the earlier analyses were freed from silver by precipitation as chloride and from oxalic acid by ignition. The columbic acid was recovered from alkaline solution by precipitation with sulphur dioxide (Sample IV).

Columbium pentachloride was prepared by treatment of the sulphide with chlorine. To prepare the sulphide, hydrogen sulphide charged with carbon disulphide was conducted over the columbic oxide at 1000°. The pentachloride was then produced by passing a current of chlorine, carefully freed from oxygen, into a nitrogen-filled glass bulb containing the sulphide and warmed to 250°. Fractional distillation of the pentachloride in an exhausted glass system followed, and the samples for analysis were sealed off in glass bulbs. Considerable difficulty was experienced at first in eliminating the higher-boiling oxychloride on the one hand and the lower-boiling sulphur chloride on the other, but this difficulty was eventually overcome.

The weight of the pentachloride was found by weighing the bulb and then, after breaking the bulb under saturated oxalic acid solution and acidification with nitric acid, the glass fragments were collected and weighed. Comparison with silver followed. All weights are corrected to vacuum.

The Atomic Weight of Columbium.

Sample.	Wt. of CbCl₅.	Wt. of Ag.	Ratio CbCl₅ : 5Ag.	At. wt. Cb.	Sample.	Wt. of CbCl₅.	Wt. of Ag.	Ratio CbCl₅ : 5Ag.	At. wt. Cb.
II	3·04386	6·07711	0·50087	92·886	III	0·94171	1·87985	0·50095	92·927
II	4·15231	8·28917	0·50093	92·918	II	0·79636	1·58976	0·50093	92·917
II	3·04987	6·08879	0·50090	92·900	II	1·03393	2·06422	0·50088	92·891
II	2·50957	5·00994	0·50092	92·910	II	1·62481	3·27968	0·50091	92·903
II	1·20611	2·40770	0·50092	92·921	IV	1·13889	2·27376	0·50088	92·892
III	0·79147	1·57998	0·50094	92·920	IV	2·48870	4·96803	0·50094	92·924
III	1·44972	2·89407	0·50093	92·915	IV	2·27453	4·54070	0·50092	92·912
							Average	0·50092	92·909

The average value of the atomic weight of columbium, 92·91, agrees almost exactly with Aston's finding that columbium is probably a simple element with an atomic weight 92·90 on the chemical scale. The value 92·91 replaces in the table the older value 93·3, which was a compromise value from earlier determinations.

MOLYBDENUM.—Lautié (*Compt. rend.*, 1933, **197**, 1730) has determined the ratio of molybdenum to its trioxide in two ways. Impure trioxide was converted into the volatile chlor-hydrine by heating in a current of dry hydrogen chloride, with rejection of the first and last portions. The product was dissolved in ammonia, and the solution evaporated to dryness. Nitric acid was then added and after heating to 400° in oxygen the residual molybdenum trioxide was five times resublimed. Portions of about 1·5 g. were heated to constant weight in a quartz boat, and then gradually to 800° in a current of activated hydrogen. The resulting metal was weighed in an atmosphere of argon or nitrogen.

In this way the ratio Mo/MoO₃ was found to be 0·66669. By reoxidation of the molybdenum the value 0·66668 was found for the same ratio. The former corresponds to the atomic weight 96·01, the latter to 96·02.

IODINE, CARBON, SODIUM.—Baxter and Hale (*J. Amer. Chem. Soc.*, 1934, **56**, 615) have compared sodium carbonate and iodine pentoxide by neutralisation. Sodium carbonate was purified by repeated crystallisation and was prepared for weighing by fusion in an atmosphere of carbon dioxide. Iodic acid was prepared from purified iodine, through potassium and barium iodates, and was fractionally crystallised until free from non-volatile residue. By gradual heating to 240°, the iodic acid was dehydrated to iodine pentoxide, and weighed. Nearly equivalent amounts of the two substances were allowed to react

in dilute aqueous solution and the resulting solution was brought to neutrality in an atmosphere free from carbon dioxide with bromothymol-blue as indicator, by adding very dilute acid and base solutions. Weights are corrected to vacuum and a correction of 0·001% for adsorbed air and of 0·0023% for retained moisture are applied to the weights of iodine pentoxide.

The Ratio of Iodine Pentoxide to Sodium Carbonate.

Wt. of Na₂CO₃.	Wt. of I₂O₅.	Ratio I₂O₅ : Na₂CO₃.	Wt. of Na₂CO₃.	Wt. of I₂O₅.	Ratio I₂O₅ : Na₂CO₃.
8·98436	28·29617	3·14949	9·29771	29·28312	3·14950
9·56078	30·11314	3·14965	9·70811	30·57533	3·14946
7·55451	23·79256	3·14945	8·42645	26·53892	3·14948
9·33412	29·39833	3·14956	8·81736	27·76915	3·14937
8·46160	26·65025	3·14955		Average	3·14950

In the following tables the atomic weights of iodine, carbon, and sodium are computed individually on the basis of various assumed atomic weights for the other two elements.

The Atomic Weight of Iodine.

	C = 12·000.	C = 12·005.	C = 12·010.
Na = 22·997	126·914	126·922	126·930
Na = 22·994	126·905	126·913	126·920

The Atomic Weight of Carbon.

	I = 126·915.	I = 126·917.	I = 126·920.	I = 126·925.
Na = 22·997	12·001	12·002	12·004	12·007
Na = 22·994	12·007	12·008	12·010	12·013

The Atomic Weight of Sodium.

	I = 126·915.	I = 126·917.	I = 126·920.	I = 126·925.
C = 12·000	22·997	22·998	22·999	23·000
C = 12·005	22·995	22·995	22·996	22·998
C = 12·010	22·993	22·993	22·994	22·995

CÆSIUM.—Baxter and Thomas (*J. Amer. Chem. Soc.*, 1934, **56**, 1108) have continued their work on the analysis of cæsium chloride, the preliminary results of which were included in the report of this Committee for 1933. Nearly four kilograms of cæsium nitrate were fractionally crystallised. The nine less soluble fractions of the last (seventeenth) series, amounting to 80% of the total material, when tested spectroscopically showed no evidence of the presence of potassium or rubidium. A portion of the combined fourth and fifth fractions was converted into perchlorate and recrystallised. The perchlorate was then converted into chloride, which was recrystallised (Sample A). The mother-liquors of Sample A were converted into dichloroiodide and after recrystallisation this salt was converted into chloride and purified as before (Sample B). Sample C was prepared from the next to least soluble of the nitrate fractions by several crystallisations as perchlorate and one as chloride. The least soluble of the nitrate fractions was recrystallised three times as perchlorate, and converted into chloride (Sample D).

The Atomic Weight of Cæsium.

Sample.	Fusion atmosphere.	Wt. of CsCl.	Wt of Ag.	Ratio CsCl : Ag.	At. wt. Cs
A	N₂	8·96291	5·74296	1·56068	132·909
A	N₂	9·60983	6·15731	1·56072	132·913
A	H₂ + 25% HCl	9·70288	6·21686	1·56074	132·916
A	H₂ + 25% HCl	9·53125	6·10698	1·56071	132·912
A	H₂	7·52304	4·82025	1·56072	132·913
B	H₂ + 75% HCl	9·38363	6·01254	1·56068	132·909
B	H₂ + 20% HCl	9·33593	5·98207	1·56065	132·906
B	H₂ + trace HCl	10·83528	6·94414	1·56035	132·874
B	N₂	7·70022	4·93415	1·56060	132·901
B	H₂ + trace HCl	7·78342	4·98770	1·56052	132·892
B	H₂ + 50% HCl	7·83724	5·02201	1·56058	132·898
C	H₂ + 35% HCl	5·78546	3·70748	1·56048	132·888
D	H₂ + 20% HCl	2·16882	1·38968	1·56066	132·907
C	H₂ + 35% HCl	4·02114	2·57655	1·56067	132·908
			Average	1·56063	132·903
		Average, excluding analysis 8		1·56065	132·906
		Average of analyses 1—7		1·56070	132·911

To prepare the chloride for weighing, it was fused in a platinum boat in various atmospheres as indicated in the table. Analysis followed the conventional method of comparison with silver. Weights are corrected to vacuum.

The value 132·91 was adopted for the International Table of 1933.

THE RARE EARTHS.—Aston (*Proc. Roy. Soc.*, 1934, **146**, 46) has determined the isotopic composition and atomic weights of the rare earths with the following results :

	Mass-spectrum values.	International values.	Difference.		Mass-spectrum values.	International values.	Difference.
Lanthanum ...	138·91	138·92	−0·01	Terbium	158·91	159·2	−0·3
Cerium	140·13	140·13	0·00	Dysprosium ...	162·5	162·46	0·0
Praseodymium...	140·91	140·92	−0·01	Holmium	164·91	163·5	+1·4
Neodymium ...	143·5	144·27	−0·8	Erbium	167·15	167·64	−0·5
Samarium	150·1	150·43	−0·3	Thulium	166·91	169·4	−0·5
Europium	151·90	152·0	−0·1	Ytterbium	173·2	173·04	+0·2
Gadolinium	156·9	157·3	−0·4	Lutecium	174·91	175·0	−0·1

While the agreement of the physical with the chemical value is in many cases as close as could be expected, in others the discrepancy is glaring. To explain the larger differences on the basis of impurity in the rare-earth material used in the chemical determinations, improbably large proportions of impurity would be required. The conventional chloride analysis used for a large proportion of the chemical determinations in many of the more favourable cases has given results agreeing closely with the physical results (lanthanum, cerium, praseodymium), so that there is no evidence against the analytical method. If the chemical result is in error, in certain cases, the difficulty may have been due to abnormal composition of the trichlorides analysed (dichlorides). It is noticeable that the discrepancies are large with many of the more complex elements (neodymium, samarium, gadolinium, and erbium), so that it seems far from certain that these determinations of mean mass with the mass spectrograph are free from error. The Committee feels that without further evidence it is impossible to decide where the difficulty lies and makes no changes in the values for this group of elements in the table.

TANTALUM.—Hönigschmid (*Naturwiss.*, 1934, **22**, 463) has analysed tantalum pentachloride, purified by sublimation in vacuum. The result for the atomic weight of tantalum, 180·89, agrees exactly with Aston's value, and is lower than the present International value. Details of this investigation were published too late for inclusion in the report for this year. Hönigschmid and Schlee (*Z. anorg. Chem.*, 1935, **221**, 129).

LEAD.—Marble (*J. Amer. Chem. Soc.*, 1934, **56**, 854) has determined the atomic weight of radiogenic lead extracted from pitchblende found near Great Bear Lake, North-West Territories, Canada. The lead was purified successively as sulphide, sulphate, sulphide, nitrate, and chloride, and the chloride was finally distilled in dry hydrogen chloride. Analysis by the conventional chloride method gave the following results. Weights are corrected to vacuum.

The Atomic Weight of Lead.

Wt. of $PbCl_2$.	Wt. of Ag.	Ratio $PbCl_2$: 2Ag.	At. wt. Pb.
2·27721	1·77393	1·283709	206·059
2·22354	1·73219	1·283658	206·048
2·22397	1·73249	1·283684	206·054
		Average 1·283684	206·054

The value found by Aston from the isotopic constitution of this same lead, when corrected to the chemical scale, is 206·08. The difference is no greater than the present accuracy of the mass spectrograph, but is greater than the apparent uncertainty of the chemical method.

RADIUM AND PROTOACTINIUM.—Two investigations on radioactive elements were published too late for inclusion in this report. Hönigschmid and Sachtleben (*Z. anorg. Chem.*, 1935, **221**, 65), using 2·2—3·5 grams of radium bromide, from the ratio $RaBr_2$: $RaCl_2$ find the atomic weight of radium to be 226·05, and v. Grosse (*J. Amer. Chem. Soc.*, 1934, **56**, 2501), from the ratio $2K_2PaF_7$ (0·07—0·09 g.) : Pa_2O_5, finds Pa = 230·6.

Batuecas (*J. Chim. Phys.*, 1934, 31, 65) takes exception to the conclusions of Cawood and Patterson concerning the densities of certain gases and their coefficients of deviation from Boyle's law. His own figures, based on average values obtained by several experimenters, are :

	Density.	$1 + \lambda.$	$M.$	
C_2H_4	1·2605(4)	1·0076(6)	28·040	C = 12·004
CO_2	1·9766(5)	1·0068(4)	44·005	C = 12·005
$(CH_3)_2O$	2·1099	1·0270	46·050	C = 12·001(5)
N_2O	1·9780	1·0073(5)	44·013	N = 14·0065
SO_2	2·9263	1·0239	64·061	S = 32·061

ATOMIC WEIGHTS, 1935.

	Symbol.	At. No.	At. wt.		Symbol.	At. No.	At. wt.
Aluminium	Al	13	26·97	Neodymium	Nd	60	144·27
Antimony	Sb	51	121·76	Neon	Ne	10	20·183
Argon	A	18	39·944	Nickel	Ni	28	58·69
Arsenic	As	33	74·91	Niobium	Nb		
Barium	Ba	56	137·36	(Columbium)	(Cb)	41	92·91
Beryllium	Be	4	9·02	Nitrogen	N	7	14·008
Bismuth	Bi	83	209·00	Osmium	Os	76	191·5
Boron	B	5	10·82	Oxygen	O	8	16·0000
Bromine	Br	35	79·916	Palladium	Pd	46	106·7
Cadmium	Cd	48	112·41	Phosphorus	P	15	31·02
Cæsium	Cs	55	132·91	Platinum	Pt	78	195·23
Calcium	Ca	20	40·08	Potassium	K	19	39·096
Carbon	C	6	12·00	Praseodymium	Pr	59	140·92
Cerium	Ce	58	140·13	Radium	Ra	88	225·97
Chlorine	Cl	17	35·457	Radon	Rn	86	222
Chromium	Cr	24	52·01	Rhenium	Re	75	186·31
Cobalt	Co	27	58·94	Rhodium	Rh	45	102·91
Copper	Cu	29	63·57	Rubidium	Rb	37	85·44
Dysprosium	Dy	66	162·46	Ruthenium	Ru	44	101·7
Erbium	Er	68	167·64	Samarium	Sm	62	150·43
Europium	Eu	63	152·0	Scandium	Sc	21	45·10
Fluorine	F	9	19·00	Selenium	Se	34	78·96
Gadolinium	Gd	64	157·3	Silicon	Si	14	28·06
Gallium	Ga	31	69·72	Silver	Ag	47	107·880
Germanium	Ge	32	72·60	Sodium	Na	11	22·997
Gold	Au	79	197·2	Strontium	Sr	38	87·63
Hafnium	Hf	72	178·6	Sulphur	S	16	32·06
Helium	He	2	4·002	Tantalum	Ta	73	181·4
Holmium	Ho	67	163·5	Tellurium	Te	52	127·61
Hydrogen	H	1	1·0078	Terbium	Tb	65	159·2
Indium	In	49	114·76	Thallium	Tl	81	204·39
Iodine	I	53	126·92	Thorium	Th	90	232·12
Iridium	Ir	77	193·1	Thulium	Tm	69	169·4
Iron	Fe	26	55·84	Tin	Sn	50	118·70
Krypton	Kr	36	83·7	Titanium	Ti	22	47·90
Lanthanum	La	57	138·92	Tungsten	W	74	184·0
Lead	Pb	82	207·22	Uranium	U	92	238·14
Lithium	Li	3	6·940	Vanadium	V	23	50·95
Lutecium	Lu	71	175·0	Xenon	Xe	54	131·3
Magnesium	Mg	12	24·32	Ytterbium	Yb	70	173·04
Manganese	Mn	25	54·93	Yttrium	Y	39	88·92
Mercury	Hg	80	200·61	Zinc	Zn	30	65·38
Molybdenum	Mo	42	96·0	Zirconium	Zr	40	91·22

181. *Electrometric Studies of the Precipitation of Hydroxides. Part XIII. The Constitution of Aqueous Solutions of Silver Oxide in Ammonia, Mono-, Di-, and Tri-methylamine and -ethylamine, Pyridine and Ethylenediamine ; with a Note on the Dissociation Constants of the Amines.*

By H. T. S. BRITTON and WILLIAM G. WILLIAMS.

COMPLEX silver–ammonia salts, $Ag(NH_3)_2X$, are formed in solution when silver salts, either soluble or insoluble, react with ammonia. They are not visibly decomposed on the addition of alkali, and the p_H values then set up indicate that little, if any, reaction can have taken place. It would appear, therefore, that the complex salts are those of strong bases, and Britton and Wilson (J., 1933, 1050) have already shown that the strong complex base, $Ag(NH_3)_2OH$, is actually formed when silver oxide is dissolved in ammonia. In the present work, we have studied the nature of the bases formed when silver oxide is dissolved in aqueous solutions of the bases specified in the title, in the hope that we might correlate the strengths of these bases with their tendencies to form co-ordinate linkages with silver. For this purpose, we employed both conductometric and potentiometric methods, and carried out a series of solubility determinations.

EXPERIMENTAL.

I. *Dissociation Constants of the Amines.*—As the dissociation constants recorded in the literature were, with one exception, obtained by methods other than potentiometric, it was considered advisable to redetermine them by means of the glass electrode—this electrode providing the only means of studying the variations in hydrogen-ion concentration during the neutralisation of the amine solutions of silver oxide. For this purpose, a series of dilute solutions of the bases were titrated with nitric acid at 18°, the glass-electrode system described by Morton (*J. Sci. Instr.*, 1930, **7**, 187) and the valve circuit introduced by Harrison (J., 1930, 1530) being used.

Table I records the p_H values obtained at different stages of typical titrations, and also the p_K values to which they correspond. The dissociation constants given in the last column are

TABLE I.

Solutions titrated.	Titrant HNO₃, N.		p_H on addition of HNO₃, c c.				Mean p_K.	K
			10	15.	20	25.		
$0.04488M$-NH₂Me (50 c c) ...	0.0660	p_H	11.11	10.87	10.62	10.32		
		p_K	3.47	3.43	3.43	3.44	3.44	3.62×10^{-4}
$0.04118M$-NH₂Et (100 c c) ...	0.1420	p_H	11.08	10.82	10.50	10.05		
		p_K	3.40	3.36	3.39	3.45	3.40	3.97×10^{-4}
$0.04910M$-NH₂Ph (50 c c) ...	0.05644	p_H	5.10	4.93	4.60	4.40		
		p_K	9.55	9.57	9.58	9.59	9.57	2.68×10^{-10}
$0.05272M$-C₅H₅N (50 c c) ...	0.05644	p_H	5.52	5.25	4.95	4.62		
		p_K	8.97	8.96	8.98	8.98	8.97	1.07×10^{-9}
$0.04256M$-NHMe₂ (50 c c) ...	0.0560	p_H	11.50	11.27	11.05	10.82		
		p_K	3.03	3.06	3.06	3.07	3.05	8.92×10^{-4}
$0.03810M$-NHEt₂ (50 c.c) ...	0.0560	p_H	11.63	11.40	11.15	10.84		
		p_K	2.81	2.82	2.83	2.86	2.84	1.45×10^{-3}
$0.04080M$-NMe₃ (50 c.c.)	0.0560	p_H	10.45	10.19	9.97	9.71		
		p_K	4.23	4.23	4.20	4.21	4.21	6.15×10^{-6}
$0.04610M$-NEt₃ (50 c.c.)	0.0560	p_H	11.49	11.25	11.05	10.87		
		p_K	3.15	3.22	3.20	3.17	3.18	6.53×10^{-4}

of the same order of magnitude as those obtained by other methods (see Landolt–Börnstein, "Physikalisch-Chemische Tabellen "). For instance, Bredig's values at 25° are : for methylamine, 5.0×10^{-4}; dimethylamine, 7.4×10^{-4}; trimethylamine, 7.4×10^{-5}; diethylamine, 1.26×10^{-3}; triethylamine, 6.4×10^{-4}; from conductivity determinations. Harned and Owen (*J. Amer. Chem. Soc.*, 1930, **52**, 5090), however, obtained 4.38×10^{-4} at 25° for methylamine by an E.M.F. method, whereas our value at 18° is 3.62×10^{-4}.

Brodig (*Z. physikal. Chem.*, 1894, **13**, 294) found the first dissociation constant of ethylene-diamine at 25° to be 8.5×10^{-5}, but the second dissociation constant has not hitherto been determined. The following data were obtained from a glass electro-titration of 50 c.c. of 0.0451M-ethylenediamine with 0.1709N-nitric acid at 18° :

HNO₃ added, c.c.	4.0	7.0	10.0	16.0	19.0	22.0
p_H	10.58	10.17	9.74	7.80	7.32	6.91
$p_{K_{b_1}}$	3.95	3.94	3.94	—	—	—
$p_{K_{b_2}}$	—	—	—	6.94	6.94	6.96

Hence $K_{b_1} = 1.14 \times 10^{-4}$ and $K_{b_2} = 1.13 \times 10^{-7}$.

II. *Solubility of Silver Oxide in Aqueous Solutions of Ammonia and Amines.*—As the solubility in ammonia has been thoroughly investigated by several workers (Whitney and Melcher, *J. Amer. Chem. Soc.*, 1903, **25**, 87; Euler, *Ber.*, 1903, **36**, 1854; Olmer, *Bull. Soc. chim.*, 1924, **35**, 333), no further determinations have been made. Their results, which are plotted in Fig. 1,

FIG. 1.

II. *Solubility of Silver Oxide in Aqueous Solutions of Ammonia and Amines.*
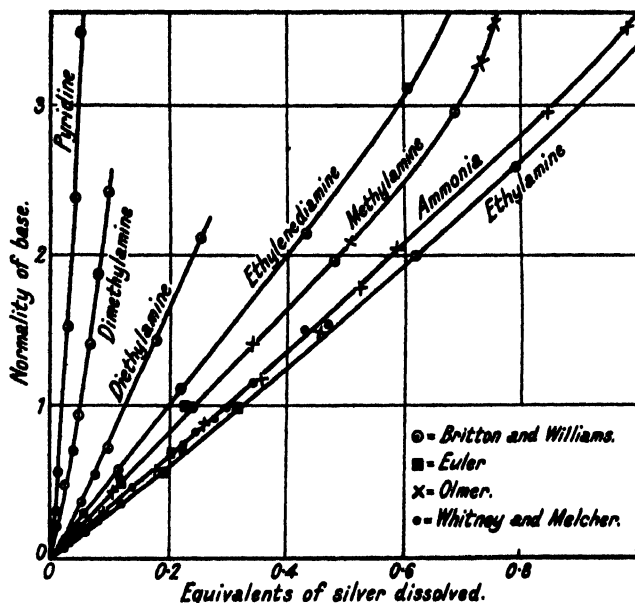
show that the amount of silver oxide dissolved is almost directly proportional to the concentration of ammonia.

A few solubility determinations of silver oxide in aqueous methylamine have been made by Olmer (*loc. cit.*) and Euler (*Ber.*, 1903, **36**, 2878).

Table II gives the results of our solubility determinations at 15° in mono-, di-, and tri-methylamine and -ethylamine, pyridine, and ethylenediamine solutions over a wide range of concentrations. The results, which are plotted in Fig. 1, yield straight lines except for the section of the methylamine curve above 2N. Attempts to measure the solubility in aqueous aniline failed owing to the oxidation which occurred.

As the solubility of silver oxide is greatly enhanced by the presence of any free acid radical left in combination with it, every precaution was taken to ensure that the silver oxide used was quite pure. It was prepared by precipitation from dilute silver nitrate solution with the stoicheiometrical amount of sodium hydroxide, washed several times with hot water until free from electrolytes, and then filtered. In case drying should cause it to lose its aptitude to dissolve, it was kept in the moist condition in a light-proof bottle. As the solutions appear to be susceptible to light, saturation was carried out in blackened bottles which were mechanically shaken at 15° until equilibrium was reached.

The silver-ion concentrations of many of these solutions were determined by means of a silver electrode, which had been covered with a crystalline electro-deposit of silver. When immersed in 0.1N-silver nitrate solution and connected through a " salt-bridge " of saturated

TABLE II.

Solubility of Silver Oxide in Aqueous Solutions of Organic Bases at 15°.

Ammonia.

NH_3, N	0·1	0·5	1·0	1·5	2·0	3·0		
Ag_2O, N	0·031	0·150	0·299	0·445	0·590	0·865		
K_I (sol.) $\times 10^6$	2·00	2·34	2·41	2·49	2·58	2·83	Mean 2·44	

Methylamine.

NH_2Me, N ...	0·0403	0·0806	0·1007	0·2014	0·5035	0·9933	1·7613	2·9611
Ag_2O, N	0·00919	0·01882	0·02338	0·04715	0·1150	0·2387	0·4107	0·6802
E.M.F. (16°)	0·178	0·163	0·157	0·142	0·121	—	—	—
$-\log [Ag^{\cdot}]$ ...	5·92	6·18	6·28	6·54	6·91	—	—	—
$K_I \times 10^6$	6·03	6·52	6·65	6·97	8·02	Mean 6·84		
K_I (sol.) $\times 10^6$	6·52	6·92	7·08	6·87	7·56	6·35	6·67	7·55 Mean 6·94

Ethylamine.

NH_2Et, N	0·07253	0·1793	0·2420	0·2500	0·3623	0·7106	2·000	2·5943
Ag_2O, N	0·2331	0·05684	0·07337	0·0798	0·1169	0·2211	0·6200	0·7926
E.M.F. (16°)	0·159	—	0·131	—	0·127	—	—	—
$-\log [Ag^{\cdot}]$ ...	6·24	—	6·75	—	6·81	—	—	—
$K_I \times 10^6$	1·78	—	2·20	—	2·40	Mean 2·13		
K_I (sol.) $\times 10^6$	1·65	1·77	2·31	1·72	1·61	1·96	2·00	2·15 Mean 1·90

Pyridine.

C_5H_5N, N	0·3020	0·5612	1·5383	2·389	3·489	
Ag_2O, N	0·0060	0·0108	0·0275	0·03905	0·0546	
K_I (sol.) $\times 10^6$	3·11	3·24	3·87	4·67	5·11	Mean 4·0

Ethylenediamine.

$C_2H_8N_2$, N ...	0·0725	0·1162	0·145	0·2905	0·572	1·101	2·149	3·111
Ag_2O, N	0·01544	0·02369	0·02947	0·05498	0·1160	0·2187	0·4480	0·6068
E.M.F. (16°)	0·176	0·166	0·159	0·141	—	—	—	—
$-\log [Ag^{\cdot}]$ ...	5·96	6·12	6·25	6·56	—	—	—	—
$K_I \times 10^7$	1·23	1·50	1·41	1·62	Mean 1·44			
K_I (sol.) $\times 10^7$	1·00	1·12	1·14	1·44	1·14	1·23	1·03	1·27 Mean 1·17

Dimethylamine.

$NHMe_2$, N ...	0·1858	0·4645	0·697	0·929	1·393	1·858	2·40
Ag_2O, N	0·00891	0·0225	0·0370	0·0459	0·0633	0·0791	0·094
E.M.F. (17°)	0·176	0·153	0·141	0·137	0·126	0·116	—
$-\log [Ag^{\cdot}]$ ...	5·93	6·33	6·54	6·61	6·80	6·97	—
$K_I \times 10^6$	3·72	3·67	3·02	3·75	3·43	3·91	Mean 3·58
K_I (sol.) $\times 10^6$	4·67	4·62	3·78	3·10	5·33	6·15	7·34 Mean 5·0

Diethylamine.

$NHEt_2$, N	0·142	0·356	0·534	0·712	1·068	1·424	2·10
Ag_2O, N	0·0212	0·0517	0·0756	0·0998	0·1281	0·1764	0·250
E.M.F. (17°)	0·164	0·137	0·134	0·126	0·112	0·108	—
$-\log [Ag^{\cdot}]$ ...	6·14	6·61	6·66	6·80	7·04	7·11	—
$K_I \times 10^7$	5·01	4·67	4·17	4·24	2·99	3·42	Mean 4·08
K_I (sol.) $\times 10^7$	2·73	3·17	2·58	3·55	5·35	4·75	5·43 Mean 4·0

Trimethylamine.

NMe_3, N	0·136	0·340	0·681	1·088	1·363	2·00
Ag_2O, N	0·00039	0·00137	0·00293	0·0043	0·0057	0·0084
E.M.F. (15°)	0·225	0·217	0·205	0·194	0·187	—
$-\log [Ag^{\cdot}]$ ...	5·13	5·25	5·48	5·67	5·80	—
$K_I \times 10^4$	3·39	4·68	5·13	5·89	5·37	Mean 4·89
K_I (sol.) $\times 10^4$	[15·3]	8·24	6·81	8·37	7·48	7·41 Mean 7·7

Triethylamine.

NEt_3, N	0·12	0·34	0·48		
Ag_2O, N	0·00164	0·00547	0·00789		
E.M.F. (15°)	0·207	0·186	0·179		
$-\log [Ag^{\cdot}]$ ...	5·44	5·81	5·93		
$K_I \times 10^5$	3·09	3·09	3·24	Mean 3·14	
K_I (sol.) $\times 10^5$	6·76	4·90	4·57	Mean 5·4	

potassium nitrate solution to a normal calomel electrode, the cell gave an E.M.F. of 0·454 volt, corresponding to $_{\epsilon}\varepsilon_{Ag} = 0·800$ volt (N-H = 0), the degree of ionisation being taken as 0·814. The E.M.F.'s recorded in Table II refer to cells : Ag | complex solution | satd. KNO_3 | N-calomel, at the temperatures indicated. The instability constants, $K_I = [Ag^{\cdot}][B]^2/[AgB_2^{\cdot}]$, were calculated therefrom, it being assumed that (i) all the silver oxide had been converted into the complex base, AgB_2OH ; (ii) the complex bases were completely ionised, thus $AgB_2OH \rightleftarrows$

$AgB_2^{\cdot} + OH'$, whence concentration of silver oxide dissolved $= [AgB_2^{\cdot}]$ g.-equivs. per litre; (iii) as the result of the ionisation of the complex base, the excesses of the different organic bases were un-ionised, and their concentrations therefore equal to [B]. In order that the "instability constant" of the ethylenediaminosilver kation might be comparable with the other constants, the concentrations of ethylenediamine have been taken in g.-equivs. per litre, so that in calculating the constants the concentrations of free ethylenediamine have been squared.

FIG. 2.

Nitric acid.
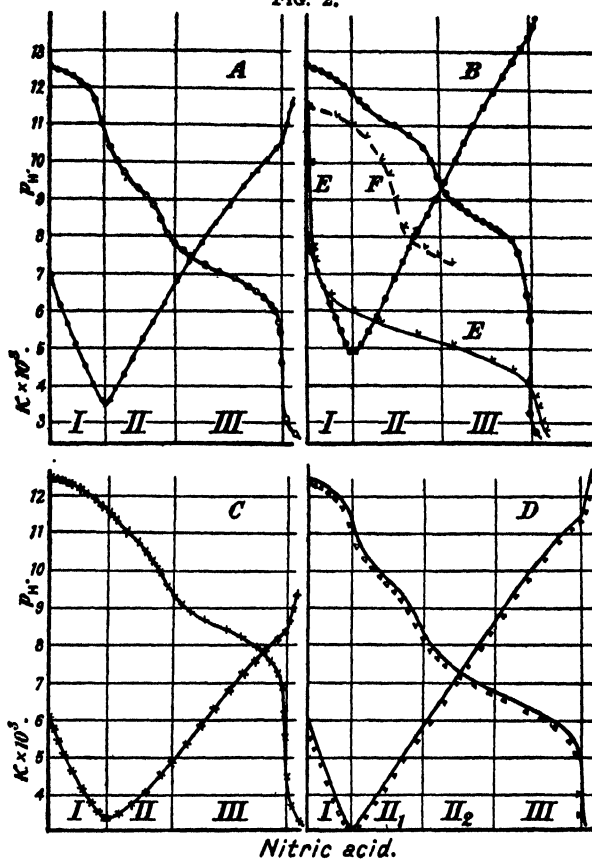
III. *Electrometric Titrations of Aqueous Solutions of Silver Oxide in Ammonia and Amines.*—Typical glass-electrode titration curves at 18° and the corresponding conductometric curves at 25° are shown in Fig. 2. The solutions employed were :

  A, 50 c.c. of $0.0298M$-$Ag(NH_3)_2OH + 0.0376N$-NH_4OH, titrated with $0.2078N$-HNO_3;
  B, 50 c.c. of $0.03920M$-$Ag(NH_2Me)_2OH + 0.0825M$-NH_2Me, titrated with $0.3380N$-HNO_3;
  C, 50 c.c. of $0.03084M$-$Ag(NH_2Et)_2OH + 0.03084M$-$NH_2Et$, titrated with $0.1928N$-HNO_3;
  D, 50 c.c. of $0.02842M$-Ag en $OH + 0.04618M$-$C_2H_8N_2$, titrated with $0.2368N$-HNO_3.

The same solutions were used to obtain the curves for κ, but 100 c.c. were used for each titration.

  Both types of curve demonstrate the formation of a strong base of the general formula $Ag(B)_2OH$, becoming Ag en OH in the case of ethylenediamine. The curves may be divided into three sections, denoted by Roman numerals, corresponding to the addition of various amounts of nitric acid : I relates to the neutralisation of the strong complex base; II to that of the ammonia or amine in excess of that required to form the complex base; and III to the decomposition of the complex nitrate, $Ag(B)_2NO_3$ (B = unhydrated base), formed at the end of stage I, into silver nitrate and the nitrate of the simple base : $AgB_2NO_3 + 2HNO_3 \rightleftharpoons AgNO_3 + 2BHNO_3$, or $AgB_2^{\cdot} + 2H^{\cdot} \rightleftharpoons Ag^{\cdot} + 2BH^{\cdot}$. Hence

$$[Ag^{\cdot}][BH^{\cdot}]^2/[AgB_2^{\cdot}][H^{\cdot}]^2 = K \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and as $B + H_2O \rightleftharpoons BH\cdot OH \rightleftharpoons BH^{\cdot} + OH'$, therefore $[BH^{\cdot}][OH']/[BH\cdot OH] = K_b$.

If it is assumed that the undissociated base is also unhydrated, *e.g.*, that undissociated ammonium hydroxide molecules exist in solution as simply molecules of ammonia (see, *e.g.*, Calingaert and Huggins, *J. Amer. Chem. Soc.*, 1923, **45**, 915), and similarly that the undissociated substituted ammonia molecules exist as such when in the un-ionised state, then the concentration of the base, [B], is equal to that of the undissociated base, [BHOH], whence

$$[BH^{\cdot}][OH']/[B] = K_b \qquad \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Combination of equations (1) and (2), and introduction of $K_w = [H^{\cdot}] \times [OH']$, give

$$[Ag^{\cdot}][B]^2/[AgB_2^{\cdot}] = K \cdot K_w{}^2/K_b{}^2 = K_I$$

where K_I is the instability constant of the complex kation in question. It is seen therefore that the p_H during stage III depends on the instability constant of the complex kation and the dissociation constant of the base which it incorporates.

That 2 equivs. of the bases combine with one of silver is apparent from the fact that the amount of nitric acid used in stage III is exactly twice the amount required in stage I. Because methylamine and ethylamine are somewhat stronger bases than ammonia, stage II in *B* and *C* tends to merge into stage I without a well-defined inflexion. The termination of the neutralisation of the strong complex methylamino- and ethylamino-silver bases is, however, clearly indicated in the conductometric curves, sharp " breaks " being obtained. No further breaks were obtained until the complex kation had been entirely decomposed and free nitric acid began to be present in the solutions. This is to be ascribed to the fact that the mobilities of the kations involved do not differ greatly from one another.

As shown in the previous section, the solubility of silver oxide in pyridine is very small. Nevertheless, the high p_H values indicated during the initial portions of curves *E* and *F* in Fig. 2, which refer to the titrations of 50 c.c. of 0·0034*M*-AgPy$_2$OH + 0·2106*M*-pyridine with 0·3368*N*-and with 0·0129*N*-nitric acid respectively, show that the complex pyridine base is quite strong.

The equivalent conductivities of the complex bases and their apparent degrees of ionisation, α, given in Table III show that the complex bases, like the silver–ammonia base (Britton and Wilson, *loc. cit.*; Whitney and Melcher, *loc. cit.*) are very strong.

TABLE III.

G.-equivs. per litre.

Base.	Base.	Ag$_2$O.	$\kappa \times 10^3$.	Λ.	p_H.	α.
Ammonia	0·0972	0·0298	—	—	12·57	0·90
Methylamine	0·1007	0·02338	4·64	189	12·48	0·78
Ethylamine	0·1210	0·03805	7·54	194	12·66	0·72
Ethylenediamine	0·1162	0·02369	4·85	202	12·47	0·78
Pyridine	0·2233	0·0034	0·620	201	11·58	0·76

The values of α were calculated from the p_H values, allowances being made for the concentrations of hydroxyl-ions originating from the excess of the organic bases; α thus represents

[Concentration of hydroxyl-ions from complex base]/[Concentration of complex base].

The specific conductivities of the small concentrations of ionised free base were calculated from the p_H values and the dissociation constants and then subtracted from the observed specific conductivities in order to find the specific conductivities caused by the complex bases and thence the equivalent conductivities.

Although the accuracy of these computations is necessarily minimised by the errors inherent in the use of the glass electrode in solutions of p_H above 12, they suffice to show (i) that the complex bases are all similar in strength to sodium hydroxide, and (ii) that the precise strength of the ammonia base bound up in the complex kation is without effect on the strength of the resulting complex base. For instance, pyridine and ethylamine are respectively the weakest and the strongest of the bases considered, yet the strengths of the complex bases are equal. Also, the widely different strengths of the two stages of dissociation of ethylenediamine appear to have no effect on their co-ordinating power.

If the previous assumptions used to interpret the p_H values set up during the third stages of the titrations *A*, *B*, and *C* (Fig. 2) are sound, then it is possible to calculate the " instability constants " of the complex ammonia, methylamine, and ethylamine kations from the dissociation constants and the ionic product of water.

The data in Table IV were obtained from the p_H values set up when 24 c.c. of titrant had been

added in each of the three titrations, which corresponds very nearly to the mid-point of the third stage. The silver nitrate was taken as completely ionised, and if suitable allowance

TABLE IV.

Titration	Salt.	Silver salt decomposed, %.	p_H observed.	K.	K_I.
A	$Ag(NH_3)_2NO_3$	51·2	7·00	$2·19 \times 10^{11}$	$3·31 \times 10^{-8}$
B	$Ag(NH_2Me)_2NO_3$	51·8	8·45	$5·62 \times 10^{14}$	$1·86 \times 10^{-7}$
C	$Ag(NH_2Et)_2NO_3$	50·0	8·40	$1·12 \times 10^{14}$	$3·72 \times 10^{-8}$

could have been made for its smaller ionisation in the presence of ammonium or substituted ammonium nitrates, the "instability constants" would have been slightly smaller. Attempts to measure the silver-ion concentrations of these solutions by the E.M.F. method did not lead to satisfactory results, apparently owing to the enhanced instability of the complex kations in such solutions, and the consequent sluggishness of the silver electrode to reach a state of equilibrium.

DISCUSSION.

Silver oxide dissolves in solutions of ammonia and amines to form strong complex bases, AgB_2OH. It is possible to explain this solubility in terms of the instability constant of the complex kation formed and the solubility product of silver hydroxide, or conversely to calculate the instability constant of the complex kation. Thus, let the concentration of base be C g.-equivs. per litre, and the amount of silver hydroxide dissolved be S g.-equivs. per litre. This is equal to the concentration of the complex base, AgB_2OH. The concentration of base which co-ordinates with the silver hydroxide is $2S$, and consequently the concentration of free base is $C - 2S$. Hence, if the degree of ionisation of the complex base, AgB_2OH, is α, then $[Ag^{\cdot}][B]^2/[AgB_2^{\cdot}] = K_I = [Ag^{\cdot}](C - 2S)^2/\alpha S$, and as the solution is saturated with respect to silver oxide, $[Ag^{\cdot}][OH'] = L$; whence $K_I = L(C - 2S)^2/\alpha S[OH']$, and as $[OH']$ originates from the ionisation of the complex base, $[OH'] = \alpha S$, and therefore $K_I = L(C - 2S)^2/\alpha^2 S^2$.

Hence $C = S(2 + \alpha\sqrt{K_I/L})$, and consequently, if α is either unity or else constant, the solubility of silver oxide should be directly proportional to the concentration of the organic base as is shown by the curves in Fig. 1. In Table II, the instability constants, K_I (sol.), obtained by means of the above formula by putting $\alpha = 1$ and taking the solubility product of silver hydroxide as $1·33 \times 10^{-8}$ (Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 531), are compared with the values obtained from potential measurements with the silver electrode. In view of the approximate nature of the assumptions involved, the agreement is satisfactory.

There appears to be no relationship between the strength of the base, as shown by the dissociation constants in Table I, and the stability of the resulting complex kations. For instance, both dimethylamine and diethylamine are stronger than either ammonia or their respective primary bases, yet the instability constants of the dialkylaminosilver kations are appreciably greater, and although pyridine is so very much weaker as a base than either of the tertiary bases trimethylamine and triethylamine, yet the pyridinosilver kation is slightly more stable than the other two. Furthermore, as will be shown in a later paper a weak primary aromatic base such as aniline gives rise to an unstable complex kation.

As far as can be ascertained from the instability constants, except for the complex aniline kation, complex kations involving ammonia or primary amines are more stable than those involving secondary amines, which in turn are more stable than those involving tertiary bases. In other words, the order of the co-ordinating tendencies with regard to silver is primary > secondary > tertiary amines.

182. *The Nature of the Ceric Sulphates.*

By Elwyn G. Jones and F. G. Soper.

The existence of the stable sulphate, $Ce(SO_4)_2$ (Meyer and Aufrecht, *Ber.*, 1904, **37**, 140; Brauner, *Z. anorg. Chem.*, 1904, **39**, 261), is largely responsible for the accepted belief in an electro-positive ceric ion. The normal nitrate has not been isolated, but only a red ceric hydroxynitrate, $Ce(OH)(NO_3)_3,H_2O$ (Meyer and Jacoby, *Ber.*, 1900, **33**, 2135). Moreover, the cerium in the " double " nitrates, $M_2Ce(NO_3)_6$, was shown (*Z. anorg. Chem.*, 1901, **27**, 359) to exist as an anion. Similarly, ceric chloride has not been isolated, but probably exists in solution as the complex acid, H_2CeCl_6, corresponding to the known series of salts, M_2CeCl_6. Brauner (*loc. cit.*) regards the complex ceroso-ceric sulphate as the cerous salt of sulphatoceric acid, $H_4Ce(SO_4)_4$, and writes its formula as $Ce^{III}HCe(SO_4)_4,12H_2O$. Praseodymium, neodymium, and lanthanum can replace the cerous atom and form analogous salts.

Brauner's formula for the ceroso-ceric sulphate suggests that ceric sulphate might be of analogous constitution, *i.e.*, $Ce^{IV}Ce(SO_4)_4$, the cerium existing partly as positive and partly as negative ions. Transport experiments have now been carried out which disprove this. The cerium in ceric sulphate solutions and in solutions of the double sulphates, $M_2Ce(SO_4)_4$, has been found always to exist as an anion. No evidence for any positive ceric ions in these sulphate solutions has been obtained. The ionisation of the solid of formula, $Ce(SO_4)_2$, must therefore be of complex character.

The usual method of preparation of this sulphate is by the action of hot concentrated sulphuric acid on ceric oxide. The sulphate does not dissolve and no reduction takes place to the cerous state (Meyer and Aufrecht, *loc. cit.*). When it is freed from sulphuric acid by washing with glacial acetic acid, its colour (Ridgeway's " Colour Standards and Colour Nomenclature," Washington, 1912) is primuline-yellow. This anhydrous sulphate is very soluble in water, and the solution on standing deposits the tetrahydrate, $Ce(SO_4)_2,4H_2O$ (Meyer and Aufrecht; Brauner, *locc. cit.*), which is sulphur- or strontium-yellow in colour (Ridgeway, *op. cit.*). From solutions of ceric sulphate in dilute sulphuric acid, a further ceric sulphate is precipitated as a pale yellow (barium-yellow) solid, and has been characterised by Spencer (*J.*, 1915, **107**, 1265) by a phase-rule method as $CeO_2,SO_3,2H_2O$. This salt was shown by Spencer to be free from cerium in the cerous condition.

The existence of these salts, coupled with the fact that cerium in solution is present only as a complex anion, suggests that cerium sulphate exists as the complex sulphatoceric acid, $H_4Ce(SO_4)_4$, or as a product of hydrolysis of this acid, $H_4[CeO_x(SO_4)_{4-x}]$. The tetrahydrate may then be represented as $H_4[Ce(OH)_4(SO_4)_2]$, and Spencer's basic salt as $H[Ce(OH)_3SO_4]$.

In the present investigation the limits of stability of the anhydrous salt and of the tetrahydrate have been examined. The latter, if dissolved in 75—100% sulphuric acid, forms a metastable solution and deposits the anhydrous salt. On the other hand, the anhydrous salt forms metastable solutions in water with evolution of heat, and such solutions, on pouring into or addition of concentrated sulphuric acid, give rise to two new sulphates, which have been characterised by Schreinemakers's method as $H_4Ce(SO_4)_4$ (English-red) and $H_2Ce(SO_4)_3$ (orange). These higher sulphates are metastable, and gradually pass into $Ce(SO_4)_2$. This conversion is rapid if the solids are washed with glacial acetic acid, in an attempt to free them from adhering sulphuric acid. The anhydrous sulphate, $Ce(SO_4)_2$, was found to be stable in contact with concentrated sulphuric acid for 3 months.

A glass-electrode titration of ceric sulphate solutions indicates that the salt, in approx. N-sulphuric acid solution, exists largely in the partially hydrolysed state as $H_2Ce(OH)(SO_4)_3$. The relative intensity of colour of the solution has been measured as a function of the sulphuric acid concentration, a Leitz colorimeter being used. The intensity increases rapidly from 0·1 to 0·4N-sulphuric acid and then remains practically constant. Temperature has a marked effect and must be carefully controlled. The diminution of colour in dilute sulphuric acid solution is probably connected with the progressive hydrolysis of the sulphatocerate anion, which results ultimately in the precipitation of the sparingly soluble basic salt $HCe(OH)_3SO_4$.

Experimental.

Methods of Analysis.—Ceric sulphate was prepared from the oxide (B.D.H., specially purified). It was freed from cerous sulphate by oxidation with sodium bismuthate (Metzger, *J. Amer. Chem. Soc.*, 1909, **31**, 523). A typical analysis of 10 c.c. of the resulting solution for CeO_2, (a) by ignition to the oxide and (b) by addition of excess ferrous sulphate solution and back-titration with permanganate, gave 0·1397 g. and 0·1402 g. CeO_2 respectively, showing that the amount of cerium present in the cerous condition was negligible. It was found that concentrated solutions of the sulphate did not yield the oxide readily on ignition, and it was best to convert the cerium into cerous oxalate (Meyer and Aufrecht, *loc. cit.*), which yields the oxide easily.

Sulphate was estimated by addition of barium chloride to a solution of the ceric compound in hydrochloric acid. Mixed crystals containing cerous and barium chlorides (Zambonini, *A.*, 1916, ii, 249) also separate, but may be removed by washing 3 times with N-hydrochloric acid. An analysis for sulphate by this method (10 c.c. gave 0·4723 g. SO_4) agreed with that obtained volumetrically by addition of excess of sodium hydroxide to the solution, thereby converting the cerium into ceric hydroxide, which was filtered off and washed, and the filtrate containing the excess of hydroxide was back-titrated with standard acid (10 c.c. gave 0·4732 g. SO_4).

Fig. 1.
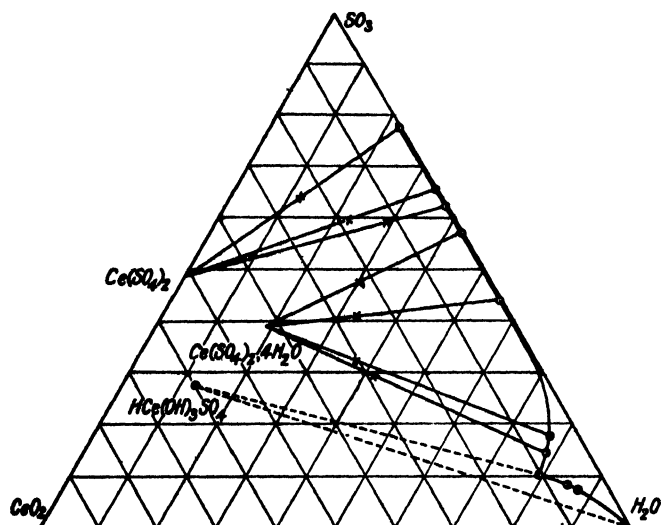
Limits of Stability of Sulphates.—Direct experiments showed that above 75% sulphuric acid, the sulphur-yellow variety of ceric sulphate, obtained by crystallisation from solution, had enhanced solubility, and deposited the primuline-yellow variety. These two types of solid were placed in stoppered bottles with sulphuric acid of different concentrations and rotated in a thermostat at 18° for 24—72 hours. The moist solids and solutions were then analysed for CeO_2 and SO_3, and the analyses plotted on the triangular diagram (Fig. 1). This characterises the sulphur-yellow solid as the tetrahydrate, and the primuline-yellow solid as the anhydrous salt. The composition of the solution in equilibrium with the basic salt, $HCe(OH)_3SO_4$, and the tetrahydrate, $H_4Ce(OH)_4(SO_4)_2$, was determined by using excess of both solid phases, and analysis of the equilibrium composition of the solution. It was not possible definitely to fix the composition of the solution in which the tetrahydrate and the anhydrous salt coexist, for equilibrium is attained only slowly at the higher acid concentrations. The composition lies, however, between 57 and 62% SO_3.

Analysis of the English-red and of the Orange Ceric Sulphates.—Addition of a concentrated solution of the metastable anhydrous salt in water to 80% sulphuric acid caused the precipitation of an orange-coloured solid. Another solid, English-red in colour, was obtained by adding concentrated sulphuric acid to the ceric sulphate solution. Of the two, the red is the more metastable, gradually passing into the orange variety before changing into the anhydrous salt. Attempts to isolate these salts, by washing with glacial acetic acid, resulted in their

decomposition into the yellow anhydrous salt. The analyses of the moist solids and of their equilibrium solutions are given below :

Analysis of orange solid.				*Analysis of red solid.*			
Moist solid.		Solution.		Moist solid.		Solution.	
CeO_2, %.	SO_3, %.	CeO_2, %.	SO_3, %.	CeO_2, %.	SO_3, %.	CeO_2, %.	SO_3, %.
22·82	63·62	0·06	74·98	24·88	62·47	0·26	71·90
23·52	61·34	0·08	70·69	24·12	63·97	0·25	75·60

For the orange solid, the resulting lines intersect at CeO_2, 40·2; SO_3, 55·0% [Calc. for $H_2Ce(SO_4)_3$: CeO_2, 39·9; SO_3, 55·8%]. For the red solid, the intersection is at CeO_2, 32·5; SO_3, 60·0% [Calc. for $H_4Ce(SO_4)_4$: CeO_2, 32·6; SO_3, 59·24%].

Electro-titration of Ceric Sulphate.—25 C.c. of a solution of ceric sulphate in sulphuric acid ($Ce^{IV} = 0·0940M$; $SO_4'' = 0·663M$) were titrated by 1·876N-sodium hydroxide with a standardised glass electrode. The valve potentiometer used was similar to that described by Harrison (*J.*, 1930, 1528). Contact was made with a calomel electrode through an agar salt

<p style="text-align:center">FIG. 2.</p>
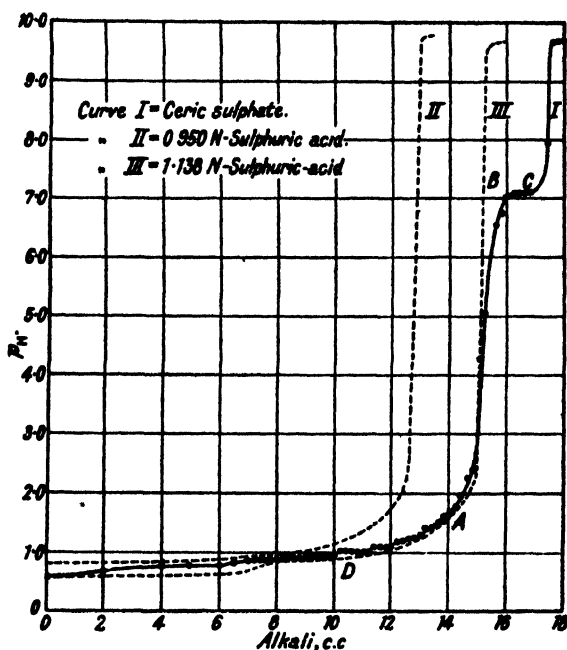
bridge. The results of the titration, converted into p_H units, are shown in Fig. 2, in which is included, for comparison, the titration of 25 c.c. of 0·950 and of 1·138N-sulphuric acid by the same alkali. The curves show that the hydrogen-ion concentration during the neutralisation of the solution of ceric sulphate conforms closely to that of 1·138N-sulphuric acid, requiring approximately 15·1 c.c. of alkali. If the ceric sulphate is completely and easily hydrolysed to $Ce(OH)_4$, the alkali required would be 17·4 c.c., but if it is partially hydrolysed to form $HCe(OH)_3SO_4$, the amount required would be 15·1 c.c. Actually, this salt begins to be precipitated at A, and the break BC corresponds to the conversion of the solid $HCe(OH)_3SO_4$ into $Ce(OH)_4$ (alkali required, 2·5 c.c.). The composition of the solid at A, B, and C was determined by analysis in duplicate experiments.

There is a slight break in the ceric sulphate curve at D, when 10·1 c.c. alkali have been added. If the ceric sulphate exists as $H_4Ce(SO_4)_4$, the free sulphuric acid in solution is 0·287M, since each cerium atom is associated with four sulphate radicals, whilst the sulphatoceric acid would be 0·376N, making the solution 0·970N in all (cf. the sulphuric acid curve). If, however, the ceric sulphate exists as $H_2Ce(OH)(SO_4)_3$, the free sulphuric acid is 0·762N, corresponding to 10·15 c.c. of alkali, and the sulphatoceric acid is 0·282N, making the solution 1·044N in all. In agreement with this calculation, the first portion of the ceric sulphate curve is intermediate

between the curves for 0·970 and for 1·138N-acid. The slight break at D coincides with the end-point of the titration of the free sulphuric acid, the partially hydrolysed sulphatoceric acid, $H_2Ce(OH)(SO_4)_2$, being assumed to be present, and may indicate that the sulphatoceric acid is a weaker acid than sulphuric. The conversion of $H_2Ce(OH)(SO_4)_2$ into $H_2Ce(OH)_2(SO_4)_2$ would require 1·25 c.c. of alkali, and there is a small but significant break on further addition of this quantity.

Intensity of Colour of Ceric Sulphate Solutions.—The relative colour intensities of solutions at 15° containing 0·0051M-ceric sulphate, $Ce(SO_4)_2$, and various concentrations of sulphuric acid are shown below :

Sulphuric acid, N	0·123	0·226	0·329	0·432	0·535	0·892
Relative intensity	0·51	0·71	0·92	1·00	1·07	1·07

Ionic-migration Experiments.—These were carried out by using a U-tube fitted with taps of bore similar to that of the tube, the bottom portion and the taps being filled with the ceric sulphate solution, and the upper portions with sulphuric acid. Solutions containing sulphuric acid from 0·5 to 20N and $Ce(SO_4)_2$ from 0·01 to 0·13M were examined over periods of 12 hours, a potential gradient of 1 volt/cm. and a current of 0·02 amp. being used. The potassium and the sodium double ceric sulphate and a mixture of ceric sulphate with lithium sulphate were also examined. In all cases, the coloured cerium ions migrated to the anode, and no evidence of any migration to the cathode was obtained.

183. *The Constitution of Sulpharsphenamine.   Part II.   A New Interpretation.*

By W. J. C. DYKE and HAROLD KING.

IN a previous communication (J., 1933, 1003) we showed that commercial sulpharsphenamines agreed in composition with a trimethylenesulphurous acid derivative of salvarsan base, and formulated sulpharsphenamine as the sodium salt of 3 : 3'-diamino-4 : 4'-dihydroxyarsenobenzene-$OO'N$-trimethylenesulphurous acid (I).

$$
\begin{array}{cc}
H_2N & NH \cdot CH_2 \cdot O \cdot SO_2H \\
SO_2H \cdot O \cdot CH_2 \cdot O\langle\ \rangle As \colon As\langle\ \rangle O \cdot CH_2 \cdot O \cdot SO_2H
\end{array} \quad (I)
$$
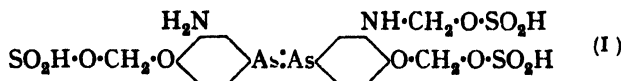
The main reasons which led to this formulation were as follows.   Newbery and Phillips (J., 1928, 116) treated the hydrochlorides of a series of anilines and o-, m-, and p-aminophenol derivatives in aqueous solution with two molecular proportions of formaldehyde, followed after a minute's interval by two molecular proportions of sodium hydrogen sulphite.   The total sulphur, by a fusion method, and the amount of sulphur oxidised to sulphate under Elvove's conditions (iodine in alkaline solution) were then determined : out of nineteen substances examined, only six showed a deficiency in sulphur oxidisable to sulphate by alkaline iodine and these six were all o-aminophenol derivatives.   In five of these six cases the atomic ratio of " unoxidised " sulphur to nitrogen approximated to unity.   It was not possible to alter this ratio by taking excess of the reagents, for, when arsphenamine was treated with four, six, or eight proportions each of formaldehyde and sodium hydrogen sulphite, the ratio of " unoxidised " sulphur to nitrogen was again unity.   In other words, o-aminophenol derivatives have the specific property of fixing one sulphur-containing group in such a way that it is not oxidised to sulphate by alkaline iodine.

We showed conclusively that the methylenesulphite groups of commercial sulpharsphenamines were part of the molecular structure.   By our distillation method of estimating methylenesulphurous acid radicals, three were found to be present, and of these three, approximately one only was oxidised to sulphate by Elvove's method.   Since we showed that crystalline mono-N-methylenesulphites of anilines and anilinearsonic acids gave a

3 G

quantitative yield of sulphate by Elvove's method, it was a reasonable deduction that in the trimethylenesulphite, sulpharsphenamine, the methylenesulphite groups which do not appear as sulphate on oxidation with alkaline iodine are present as *O*-methylenesulphite groups. Such an interpretation was supported by the results of hydrolysis by hydrochloric acid at 0°, a monomethylenesulphite being precipitated in which the whole of the sulphur could be oxidised to sulphate by alkaline iodine.

We realised, however, that our interpretation of the results was open to criticism, for no *O*-methylenesulphites of phenolic substances were known and our own attempts to prepare such failed, and in addition ·it was very surprising that *O*-methylenesulphite groups, in contradistinction to *N*-methylenesulphite groups, should not be oxidised to sulphate by Elvove's method. No alternative explanation could, however, be devised which would reconcile the results of Newbery and Phillips with our own.

In development of our programme of study of the correlation of the therapeutic properties with degree and type of substitution in the group of methylenesulphoxylate and methylenesulphite derivatives of arsphenamine base we attempted to prepare a fully substituted *OO'NN'*-tetramethylenesulphite of salvarsan base by the action of six molecular proportions of formaldehyde followed by six molecular proportions of sodium hydrogen sulphite. The solid product was a typical sulpharsphenamine and on analysis it yielded the following results, which are expressed as atomic ratios. In the second row are the results of the analysis of the product precipitated from an aqueous solution of this sulpharsphenamine by glacial acetic acid, a reagent which allows of the separation of any inorganic salts present.

TABLE I.

	As.	Total S	Oxidised S (Elvove).	Unoxidised S.	CH_2O.
Original product	2	3·6	0·43	3·2	3·3
After $CH_3 \cdot CO_2H$	2	3·3	0·54	2·8	3·2

This table shows that there are more than three combined methylenesulphite radicals in the product and of these, almost three escape oxidation to sulphate by Elvove's method. On the basis of the views we have developed, these three groups should be attached to phenolic hydroxyl groups, of which only two are available. This result is typical of several such products obtained with a high degree of substitution and it necessitated a critical re-examination of the problem of the constitution of sulpharsphenamine.

In our earlier communication we recorded unsuccessful attempts made to prepare crystalline methylenesulphites of *o*-aminophenol derivatives which would show the Elvove anomaly. We have now isolated three crystalline dimethylenesulphites of suitable *o*-aminophenol derivatives. When 4-nitro-2-aminophenol (II) in hydrochloric acid solution is treated with four molecular proportions of formaldehyde for 60 seconds, followed by four molecular proportions of freshly prepared sodium hydrogen sulphite, a clear solution is obtained from which, after removal of the sulphur dioxide by aspiration and subsequent neutralisation, a very soluble crystalline *dimethylenesulphite* of *4-nitro-2-aminophenol* can be isolated by fractional crystallisation but with considerable difficulty. By making use, however, of a chance observation that this dimethylenesulphite reacts with another molecule of sodium hydroxide to yield a *trisodium* derivative which crystallises well from solutions rich in methyl alcohol, it was possible to isolate from the original reaction mixture a pure substance $C_8H_7O_9N_2S_2Na_3,2H_2O,1\frac{1}{2}MeOH$, in 87% yield. A portion of the methyl alcohol is retained on drying at 120° and is essential for crystallisation of this salt, since

OH   O·CH_2·O·SO_2Na   OH

⟨NH_2⟩   ⟨NH·CH_2·O·SO_2Na⟩   ⟨N<CH_2·O·SO_2Na / CH_2·O·SO_2Na⟩

NO_2   NO_2   NO_2

(II.)   (III.)   (IV.)
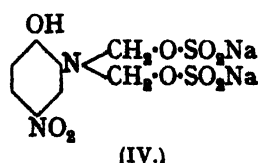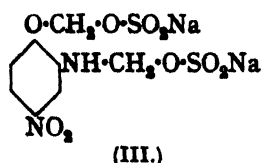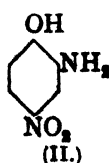
no crystallisation occurs with other alcohols. When this trisodium salt is neutralised with one equivalent of hydrochloric acid, the previously mentioned dimethylenesulphite of
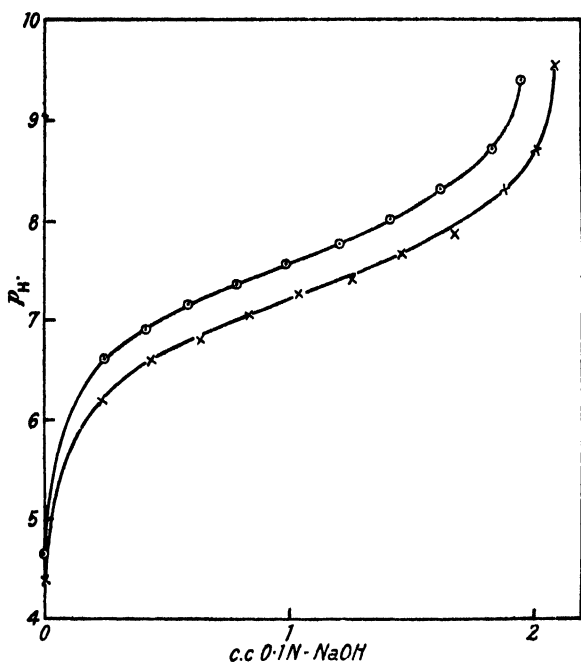
4-nitro-2-aminophenol can be isolated in 84% yield. There are only two possible formulæ, (III) and (IV), for such a dimethylenesulphite, and the observation that it can form a tri-sodium salt is in favour of formula (IV). This constitution is substantiated by a comparison of the results of electrometric titration (see Fig.) of this dimethylenesulphite with those obtained with the corresponding *mono*-N-*methylenesulphite* of 4-*nitro-2-aminophenol* (V) by means of the glass electrode. For this determination we are indebted to our colleague, Dr. W. J. Elford.

OH
NH·CH₂·O·SO₂Na
NO₂
(V.)

OH
NO₂—N<CH₂·O·SO₂Na / CH₂·O·SO₂Na
(VI.)

OH
N<CH₂·O·SO₂Na / CH₂·O·SO₂Na
CO₂Me
(VII.)
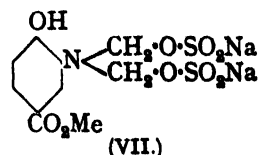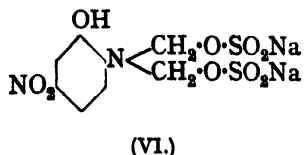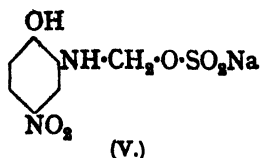
From 5-nitro-2-aminophenol hydrochloride and from 4-carbomethoxy-2-aminophenol hydrochloride by condensation with formaldehyde and sodium hydrogen sulphite in succession it has been found possible, but again with considerable difficulty, to isolate both the *mono*-N-*methylenesulphites* and the *di*-NN-*methylenesulphites* (VI) and (VII) respectively in the crystalline state. Since (VII) was a colourless substance, it could be titrated with 0·1N-alkali and thymolphthalein; it consumed approximately one equivalent of alkali —an observation also in support of the assigned structure.

Crystalline dimethylenesulphite derivatives of substituted *o*-amino-phenols of known constitution now being available, a close study was made of the applicability of Elvove's method of oxidation to these substances. 2-Hydroxy-5-nitroanilino-*NN*-dimethylenesulphite (IV), when oxidised by alkaline iodine, gave erratic results, for out of a total of 14·2% of sulphur found by distillation and estimated as barium sulphate, the amount found by Elvove's method ranged between 6·9 and 9·2% and thus bore no stoicheio-metric relation to the total sulphur or the nitrogen content of the parent substance. The *NN*-dimethylenesulphites (VI) and (VII) gave 61 and 64% respectively of their sulphur as sulphate under Elvove's conditions.

Upper curve : sodium 5-nitro-2-hydroxyanilino-N-methylenc-sulphite (0·0594 g. in 5 c.c.).
Lower curve : disodium 5-nitro-2-hydroxyanilino-NN-dimethylenesulphite (0·0902 g. in 5 c.c.)

The striking observation that the sulphur in a mono-*N*-methylenesulphite should behave in a different way from that in an *NN*-dimethylenesulphite made it necessary to inquire into the fate of the sulphur which escaped oxidation to sulphate. For this purpose the highly substituted experimental sulpharsphenamine (p. 806) proved very suitable, since only 12% of its sulphur appears as sulphate·on oxidation with alkaline iodine. On examination of the acid filtrate after quantitative separation of barium sulphate it was found that, if more hydrochloric acid was added and the solution was boiled down for ¼ hour, there was no visible precipitate, but if boiled down still further for an additional 1·5 hours there was a copious separation of barium sulphate. If to the original acid filtrate of a control experiment the same amount of hydrochloric acid was added, followed

by a quantity of sulpharsphenamine equal to the starting material and the solution boiled, then within 10 minutes there was a marked appearance of barium sulphate and after 30 minutes' boiling 65% of the sulphur introduced had appeared as sulphate. These experiments demonstrate that the " unoxidised " sulphur under the Elvove conditions cannot be present as sulphite or methylenesulphite, but must be present in a form which on prolonged digestion with mineral acid yields sulphate. The only explanation which covers the observations is that the missing sulphur is present as dithionate. The analytical detection of dithionates usually depends on the formation of sulphur dioxide and sulphuric acid without separation of any elementary sulphur when a solution is boiled with moderately strong mineral acid. The detection of sulphurous acid is not possible in our solutions owing to the presence of oxidising agents, but the way in which barium sulphate appears is exactly paralleled by control dithionate solutions containing barium ions. We also find that dithionate is not converted into sulphate by alkaline iodine. It is generally agreed that the sulphur atoms in dithionates are linked together and we suggest that it is the proximity of the two methylenesulphite groups which favours dithionate formation. The action of alkaline iodine on these NN-dimethylenesulphites of o-aminophenols is therefore a dual action, a portion of the sulphur being oxidised to sulphate and a portion to dithionate.

$$\text{(structure)} \quad \longrightarrow \quad \left[\text{O}_2\text{S O}_2\right]\text{Na}_2 \quad + \quad \left[\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O}\right]\text{Na}_2$$
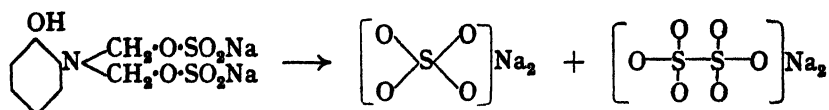
It is a remarkable observation that in the case of a highly substituted sulpharsphenamine as much as 88% of the methylenesulphite groups should appear as dithionate, a reaction which has no counterpart in inorganic chemistry where dithionate formation from sulphites and iodine plays but a minor rôle (Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X, 579; compare, however, Sokoloff and Maltschewsky, *J. Russ. Phys. Chem. Ges.*, 1881, **1**, 169).

On our present view commercial sulpharsphenamine conforming to B.P. 1932 corresponds approximately to a sodium salt of 3 : 3'-diamino-4 : 4'-dihydroxyarsenobenzene-NNN'-trimethylenesulphurous acid (VIII)

$$\text{HO}\langle\quad\rangle\text{As}=\text{As}\langle\quad\rangle\text{OH} \quad \text{NH·CH}_2\text{·O·SO}_2\text{H} \quad \text{N}\!\!<\!\!\begin{array}{l}\text{CH}_2\text{·O·SO}_2\text{H}\\\text{CH}_2\text{·O·SO}_2\text{H}\end{array} \quad \text{(VIII)}$$
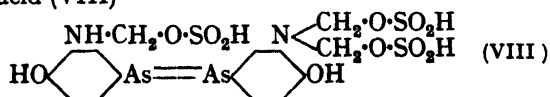
and the whole of our experimental observations both in this communication and in our previous one are in agreement with this structure. In particular the observation that 4-nitro-2-aminophenol hydrochloride, when allowed to react in succession with four molecular proportions of formaldehyde and sodium hydrogen sulphite, gives at least an 87% yield of an NN-dimethylenesulphite is an indication that the main attack in such circumstances falls on the amino-groups, and the same probably applies to arsphenamine when subjected to the same treatment.

There remained only one outstanding difficulty, that of explaining why the Elvove phenomenon according to Newbery and Phillips's experimental results should be confined to o-aminophenol derivatives. This necessitated a repetition of the work of Newbery and Phillips on aniline, o-anisidine, o-aminophenol, p-aminophenol, 4-amino-2-hydroxyphenylarsonic acid, and arsphenamine, with the result that we failed to substantiate their findings. On the contrary we find that anilines in general, when treated in acid solution with two molecular proportions of formaldehyde, followed by sodium hydrogen sulphite, yield a solution in which the whole of the sulphur can be estimated by our distillation method for methylenesulphite groups, but when examined by Elvove's alkaline iodine method show a marked deficiency in the amount of sulphur found as sulphate. In fact, aniline, o-anisidine, o-aminophenol and p-aminophenol show a deficiency of sulphur appearing as sulphate amounting to somewhere between 0·5 and 1·1 atoms of sulphur. Furthermore the ratio of " unoxidised " sulphur, that is, sulphur not appearing as sulphate, to nitrogen in the case of arsphenamine does increase with increasing proportions of formaldehyde
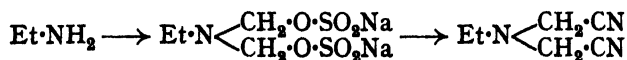
and sodium hydrogen sulphite and may be considerably more than unity. The Elvove phenomenon is thus not a specific property of o-aminophenol derivatives but of anilines in general.

It follows that it should be possible to isolate NN-dimethylenesulphites of anilines containing no hydroxyl groups by the action of formaldehyde and sodium hydrogen sulphite in succession on their hydrochlorides. This we have been able to accomplish quite readily in the only case so far examined, namely, m-nitroaniline. As might now be expected, *disodium 3-nitroanilino-NN-dimethylenesulphite* shows the Elvove phenomenon in striking fashion.

In conclusion, the results recorded in our previous communication and those just described enable us to say that anilines in general, when condensed with preformed sodium formaldehydebisulphite, form almost exclusively mono-N-methylenesulphites in which the whole of the sulphur can be found as sulphate when oxidised by alkaline iodine; but if their hydrochlorides are treated at room temperature with excess of formaldehyde, followed by sodium hydrogen sulphite, the product is mainly the NN-dimethylenesulphite in which only a portion of the sulphur can be oxidised to sulphate by alkaline iodine.

$$\text{Sulphate and dithionate} \xleftarrow{\text{NaOH} + \text{I}_2} \underset{\xrightarrow[\text{CH}_2\text{O} + \text{NaHSO}_3]{}}{\overset{\xleftarrow{\text{(HCl)}}}{\text{N}\begin{cases}\text{CH}_2\cdot\text{O}\cdot\text{SO}_2\text{Na}\\\text{CH}_2\cdot\text{O}\cdot\text{SO}_2\text{Na}\end{cases}}} \quad \text{NH}_2 \xrightarrow{\text{CH}_2(\text{OH})\cdot\text{SO}_3\text{Na}} \text{NH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_2\text{Na} \xrightarrow{\text{NaOH} + \text{I}_2} \text{Sulphate}$$
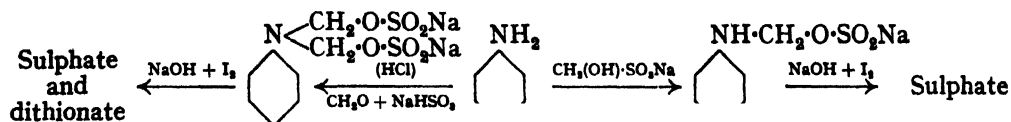
It is possible that these observations, which have led to the discovery of a new class of compounds, may have important technical application. It is of interest that with an aliphatic amine a dimethylenesulphite may be formed by the action of preformed formaldehydebisulphite, for Knoevenagel and Mercklin (*Ber.*, 1904, **37**, 4093) record the isolation of a 73% yield of ethyliminobisacetonitrile by treating ethylamine with sodium formaldehydebisulphite, followed by potassium cyanide. The reaction may be represented in this way :

$$\text{Et}\cdot\text{NH}_2 \longrightarrow \text{Et}\cdot\text{N}\begin{cases}\text{CH}_2\cdot\text{O}\cdot\text{SO}_2\text{Na}\\\text{CH}_2\cdot\text{O}\cdot\text{SO}_2\text{Na}\end{cases} \longrightarrow \text{Et}\cdot\text{N}\begin{cases}\text{CH}_2\cdot\text{CN}\\\text{CH}_2\cdot\text{CN}\end{cases}$$

A study of the action of potassium cyanide and other reagents on the NN-dimethylenesulphites of anilines should lead to results of interest.

EXPERIMENTAL.

Sodium 5-Nitro-2-hydroxyanilino-N-methylenesulphite (V).—4-Nitro-2-aminophenol (4·6 g.) was condensed with sodium formaldehydebisulphite (9 g., 2 mols.) in water (20 c.c.) at 70—75° for 30 minutes, and the resulting deep red solution concentrated over sulphuric acid in a vacuum until crystallisation set in. The product (8·6 g.), twice recrystallised from 0·7 part of water, separated in orange-red feathery needles. From two preparations different *hydrates* were obtained, one having 2¼ molecules of water [Found : S(Elvove), 10·2; S(volatile), 10·4; CH$_2$O, 9·3; H$_2$O at 120°, 13·6. C$_7$H$_7$O$_6$N$_2$SNa,2¼H$_2$O requires S, 10·2; CH$_2$O, 9·5; H$_2$O, 14·3%] and the other 1¼ molecules of water of crystallisation [Found : Na, 7·7; S(Elvove), 10·6, 10·5; H$_2$O at 120°, 9·3. C$_7$H$_7$O$_6$N$_2$SNa,1¼H$_2$O requires Na, 7·7; S, 10·8; H$_2$O, 9·1%].

Disodium 5-Nitro-2-hydroxyanilino-NN-dimethylenesulphite (IV).—4-Nitro-2-aminophenol (10 g.) in 2N-hydrochloric acid (32·5 c.c., 1 mol.) was treated with 40% aqueous formaldehyde (20 c.c., 4 mols.) for 1 minute; a gummy solid then separated in quantity. On addition of sodium hydrogen sulphite solution (4 mols.), freshly prepared by saturating an aqueous solution of 13·8 g. of anhydrous sodium carbonate in water (55 c.c.) with sulphur dioxide, a clear solution was obtained in a few minutes. Excess of sulphur dioxide having been removed by aspiration, the solution was neutralised with 50% sodium hydroxide solution and filtered, and 50% sodium hydroxide solution (5·2 c.c., 1 mol.) added (total volume now 115 c.c.), followed by warm methyl alcohol (120 c.c.). The orange-red needles obtained (24·8 g.) were collected after 24 hours and washed with 50 c.c. of 80% methyl alcohol. The filtrate and washings on further dilution with pure methyl alcohol gave a further 3·15 g. The product was *trisodium 5-nitro-2-hydroxyanilino-NN-dimethylenesulphite* free from chloride, sulphite, or sulphate. It can be recrystallised with very little loss by solution in an equal weight of warm water and addition of 5 vols. of warm

methyl alcohol [Found : Na, 14·2; S(volatile), 13·2; S(Elvove), 6·45, 6·15; OMe, 7·9, 8·1; CH_2O, 11·5; loss at 120°, 10·7. $C_8H_7O_9N_2S_2Na_3,2H_2O,1\frac{1}{2}CH_3\cdot OH$ requires Na, 14·0; S, 13·0; OMe, 9·4; CH_2O, 12·2; loss of $2H_2O,\frac{1}{2}CH_3\cdot OH$, 10·6%. Found for solid dried at 120° : OMe, 4·9, 5·3, 5·2. $C_8H_7O_9N_2S_2Na_3,CH_3\cdot OH$ requires OMe, 7·0%].

For conversion into the disodium salt the trisodium salt (19·7 g.) was treated with *N*-hydrochloric acid (37·5 c.c.) until the solution was neutral to litmus. The clear solution was evaporated in a vacuum over sulphuric acid until there was a copious crystallisation, then warmed to dissolve all salts, and allowed to crystallise at 0°. The *disodium* salt separated in clusters of large bold orange prisms (12·8 g.). It contained a trace of chloride, removable by recrystallisation from 0·6 part of warm water. Owing to the difficulty of removing larger quantities of sodium chloride when present it is preferable to recover the trisodium salt by the methyl alcohol method described above. In this way from the mother-liquors of the disodium salt a crop of pure trisodium salt (3·0 g.) was recovered, making the yield of disodium salt on trisodium salt used, 84% [Found : Na, 9·9; S(volatile), 14·4; S(Elvove), 7·0, 7·5; loss at 120°, 13·4. $C_8H_8O_9N_2S_2Na_2,3\frac{1}{2}H_2O$ requires Na, 10·2; S, 14·3; H_2O, 14·0%].

Disodium 5-nitro-2-hydroxyanilino-*NN*-dimethylenesulphite has also been isolated without making use of the trisodium salt. By laborious fractional crystallisation of the neutralised solution obtained from 4-nitro-2-aminophenol monohydrate (10·3 g.) condensed as previously described, the disodium salt (1·5 g.) was obtained as small, pale orange-yellow prisms [Found : C,* 21·5, 21·5; H,* 3·5, 3·6; N*, 6·1, 6·3; Na, 10·0; S(volatile), 14·3; S(Elvove), 7·9; CH_2O, 12·5; H_2O at 120°, 13·4. Calc. : C, 21·4; H, 3·4; N, 6·2; Na, 10·2; S, 14·3; CH_2O, 13·4; H_2O, 14·0%].

Sodium 4-nitro-2-hydroxyanilino-N-methylenesulphite (6·75 g.), prepared by the condensation of 5-nitro-2-aminophenol (3·1 g.) with sodium formaldehydebisulphite (6 g., 2 mols.) in water (10 c.c.) at 100° for 30 minutes and subsequent concentration in a vacuum, crystallised from water (5 c.c.) in rectangular, pale orange-brown prisms (4·9 g.) of a *trihydrate* [Found : Na, 7·1; S(volatile), 10·1; S(Elvove), 9·7; CH_2O, 8·8; H_2O at 120°, 15·0. $C_7H_7O_6N_2SNa,3H_2O$ requires Na, 7·1; S, 9·9; CH_2O, 9·2; H_2O, 16·7%].

Disodium 4-Nitro-2-hydroxyanilino-NN-*dimethylenesulphite* (VI).—Addition of 40% formalin (18 c.c., 4 mols.) to a solution of 5-nitro-2-aminophenol (9·3 g.) in *N*-hydrochloric acid (120 c.c., 2 mols.) caused an immediate formation of a yellow precipitate. After 30 seconds, 35% sodium hydrogen sulphite solution (68 c.c., 4 mols.) was added and, on shaking, the precipitate completely dissolved. After removal of free sulphur dioxide by aspiration the solution was neutralised, concentrated to a small volume under reduced pressure at 50°, and kept at 0°. Sodium chloride separated first and after filtration the red liquor was concentrated to a syrup, which gradually deposited crystalline material (24·9 g.). After several recrystallisations each time from 0·3 part of water the pure NN-*dimethylenesulphite* (1 g.) was obtained [Found : N, 6·4; Na, 10·9; S(volatile), 14·95; S(Elvove), 10·1; CH_2O, 13·3; H_2O at 120°, 5·8. $C_8H_8O_9N_2S_2Na_2,2\frac{1}{2}H_2O$ requires N, 6·5; Na, 10·7; S, 14·9; CH_2O, 13·9; loss of $1\frac{1}{2}H_2O$, 6·3%]. This salt crystallises in golden rectangular plates from water, in which it is many times more more soluble than the corresponding mono-*N*-methylenesulphite and is therefore freed from other salts only with great difficulty. The original mother-liquor deposited small crops, 3·1 g. in all, of a substance which on recrystallisation from water gave pure sodium 4-nitro-2-hydroxyanilino-*N*-methylenesulphite trihydrate identical with that described above [Found : S(volatile), 10·2; CH_2O, 9·0. Calc. : S, 9·9; CH_2O, 9·2%].

Disodium 2-Hydroxy-5-carbomethoxyanilino-NN-*dimethylenesulphite* (VII).—To a solution of methyl 3-amino-4-hydroxybenzoate (10 g.) in *N*-hydrochloric acid (60 c.c., 1 mol.), 40% formalin (18 c.c., 4 mols.) was added, followed in 40 seconds by 35% aqueous sodium hydrogen sulphite (70 c.c., 4 mols.). The yellow precipitate dissolved on shaking and the free sulphur dioxide was removed by aspiration. The neutralised solution was filtered, and concentrated to a thick syrup in a vacuum. After removal of some sodium chloride, the syrup deposited crystals (24·5 g.), which on recrystallisation from water (10 c.c.) gave a small crop (1·3 g.) which crystallised from water (0·6 c.c.) in characteristic elongated plates (0·6 g.) of sodium 2-hydroxy-5-carbomethoxyanilino-*N*-methylenesulphite (J., 1934, 1715) [Found : S(volatile), 10·2; CH_2O, 8·9. Calc. : S, 10·0; CH_2O, 9·4%]. From the first recrystallisation mother-liquor after removal of further quantities of the mono-*N*-methylenesulphite a larger crop (7·8 g.) was obtained. In two recrystallisations from 0·3 part of water the required NN-*dimethylenesulphite dihydrate* was obtained in extremely fine, colourless, hair-like needles [Found : N, 3·1; Na, 10·7; S(volatile),

14·9; S(Elvove), 9·1; CH₂O, 12·65; H₂O at 120°, 8·5. C₁₆H₁₁O₆NS₂Na₂,2H₂O requires N, 2·2; Na, 10·6; S, 14·7; CH₂O, 13·8; H₂O, 8·3%]. On titration with thymolphthalein as indicator, 0·1 g. required 2·20 c.c. of 0·1N-sodium hydroxide, the calculated value for one phenolic group being 2·30 c.c. For comparison 0·1 g. of the mono-N-methylenesulphite required 3·13 c.c. of 0·1N-sodium hydroxide, corresponding to complete neutralisation of the phenolic group, the calculated value being 3·13 c.c.

Sodium 3-Nitroanilino-N-methylenesulphite.—*m*-Nitroaniline (3·5 g.), sodium formaldehyde-bisulphite (7·5 g.), and water (20 c.c.) were gently boiled together until solution was effected and then kept at 90° for 1 hour. The condensation product (5·5 g.) crystallised readily. It was twice recrystallised from 2 parts of water and separated as a *dihydrate* crystallising in dense clusters of small yellow plates [Found : Na, 7·7; S(volatile), 11·0; S(Elvove), 11·2; CH₂O, 10·0; H₂O at 120°, 12·1. C₇H₇O₅N₂SNa,2H₂O requires Na, 7·9; S, 11·0; CH₂O, 10·3; H₂O, 12·4%].

Disodium 3-Nitroanilino-NN-dimethylenesulphite.—A solution of *m*-nitroaniline (6·9 g.) in N-hydrochloric acid (57 c.c.) was treated with 40% formalin (11·25 c.c., 3 mols.), immediate precipitation of a yellow solid occurring. After 60 seconds a solution of sodium hydrogen sulphite (3 mols.) prepared from anhydrous sodium carbonate (8 g.) in water (30 c.c.) was added; after a short time the precipitate dissolved. Free sulphur dioxide was removed, and the solution neutralised to litmus. On concentration a crop (17·2 g.) of a reddish-yellow crystalline solid was obtained containing some sodium chloride. The latter can be removed by several recrystal-lisations from water, but more readily by dissolving the crude solid in 0·5 part of warm water and adding 9 parts of methyl alcohol. On keeping, the NN-*dimethylenesulphite* crystallised in long silky yellow needles containing one molecule of methyl alcohol of crystallisation which is only partly lost at 120° [Found : N, 6·9; Na, 11·3; S(volatile), 15·7; S(Elvove), 8·3; CH₂O, 14·1; OMe, 6·2; loss at 120°, 3·3. C₈H₈O₈N₂S₂Na₂,MeOH requires N, 7·0; Na, 11·4; S, 15·9; CH₂O, 14·9; OMe, 7·7%]. Further quantities can be isolated from the aqueous methyl-alcoholic mother-liquor by careful addition of dry ether.

Highly Substituted Sulpharsphenamines.—In the following preparations the method of Christiansen (*J. Amer. Chem. Soc.*, 1923, **45**, 2184) was followed, 3·66 g. of the same stock of arsphenamine base being employed in each case. After condensation the products were pre-cipitated by 5 vols. of alcohol. Products B and C were preparations which had been reprecipit-ated in the same way. The products were in each case typical sulpharsphenamines showing the phenomenon of delayed precipitation by excess of mineral acid. The analytical data and atomic ratios are recorded in the following table :

Prepn.	CH₂O and NaHSO₃ equiv.	As, %.	Volatile S, %.	Elvove S, %.	Free SO₄″ S, %.	CH₂O, %.	Atomic Ratios. As	Volatile S	Oxidised S	: S by diff.	Unoxidised : CH₂O
A	4	19·3	12·1	2·8	0·25	11·2	2	2·9	0·6	: 2·3	2·9
B	6	18·1	14·0	1·9	0·3	12·0	2	3·6	0·4	: 3·2	3·3
C	8	19·1	12·6	2·2	0·4	11·4	2	3·1	0·45	: 2·65	3·0

Preparation B was dissolved in water (2 g. in 5 c.c.), and the solution cooled in ice. With rapid stirring, glacial acetic acid (40 c.c.) was added, and the precipitate collected, washed with acetic acid and then alcohol. The product (1·8 g.), dried in a high vacuum, was a pale yellow powder easily soluble in water [Found : As, 17·2; S(volatile), 12·2; S(Elvove), 2·0; CH₂O, 11·1, whence As : S(volatile) : S(oxidised) : S(unoxidised, by diff.) : CH₂O = 2 : 3·3 : 0·5 : 2·8 : 3·2]. This experiment shows that practically the whole of the sulphur in preparation B is in the form of combined methylenesulphite groups and that about 88% is not found as sulphate on oxidation with alkaline iodine.

It is instructive to compare the analyses of preparations A, B and C with those given for commercial sulpharsphenamines (J., 1933, 1005).

Elvove's Oxidative Method of Analysis and its Limitations.—In the original directions given by Elvove (*U.S. Pub. Health Rep.*, 1925, **40**, 1235) an aqueous solution of the substance (0·1 g.) is treated with 0·1N-iodine (50 c.c.), followed by N-sodium hydroxide (20 c.c.). After 5 minutes the excess of iodine is liberated by addition of N-hydrochloric acid (21 c.c.) and then removed by the addition of sufficient 0·05M-sodium arsenite. Another 5 c.c. of N-acid are added, and the sulphate in the solution then estimated as barium sulphate.

Elvove employed the reaction for the analysis of neoarsphenamine and sulpharsphenamine. In the former case all the sulphur except the so-called nuclear sulphur, but in the latter only a portion, was oxidised to sulphate. Elvove expressed the opinion that in the latter case it was only uncombined sodium formaldehydebisulphite which had its sulphur oxidised to sulphate,

In our previous communication we showed that this view was incorrect, since mono-*N*-methylene-sulphites of various substituted anilines give up the whole of their sulphur as sulphate.

In our attempts to clear up the anomaly discovered by Elvove in the case of sulpharsphen-amine we examined the Elvove conditions closely and tried the effect of varying the numerous factors involved. Although Elvove found that 5 minutes was sufficiently long in the case of sulpharsphenamine for the alkaline iodine to exert its maximum effect, our experience with pure crystalline *p*-aminophenylarsono-*N*-methylenesulphurous acid (J., 1933, 1009) leads us to believe that as a general process for *N*-methylenesulphites 5 minutes' oxidation is insufficient, but that after 1 hour oxidation is complete [Found : S(Elvove conditions, 5 mins. oxidation), 8·3, 6·9; S(1 hour's oxidation), 10·4. Calc., 10·3%]. In all our analyses, therefore, the alkaline iodine has been allowed to react for 1 hour.

In the case of the sulpharsphenamines where the Elvove anomaly appears, the effect of varying the conditions was very instructive. Using preparation A recorded above, where the proportion of sulphur appearing on oxidation as sulphate is very small, we obtained the following results : Ordinary Elvove quantities, 1 hour at 20°, S, 2·8%; 16 hours at 20°, S, 2·9%; 16 hours at 37°, S, 2·9%. If, however, the substance was kept, with 20 c.c. of *N*-sodium hydroxide only, for 16 hours at 20°, and then for 1 hour after the addition of 50 c.c. of 0·1*N*-iodine, almost all the sulphur appeared as sulphate [Found : S, 11·7%, by distillation method 12·1%]. Another preparation of a sulpharsphenamine gave with the ordinary Elvove quantities, time 1 hour, S, 3·1; 3·3%. When the quantity of iodine was increased to 60 c.c. and oxidation carried out for 16 hours, the sulphur found as sulphate was 2·9%, and when the quantity of iodine and alkali was doubled and the time of oxidation 16 hours the sulphur found as sulphate was 3·5%.

For sulpharsphenamines, therefore, the Elvove method gives consistent results independent of time, quantity of reagents or temperature, but *N*-alkali alone, given sufficient time, hydrolyses practically the whole of the combined methylenesulphite groups, which ensures their conversion into sulphate.

When the Elvove method was applied to the analysis of crystalline disodium 5-nitro-2-hydroxyanilino-*NN*-dimethylenesulphite (IV), erratic results varying between S, 6·9 and S, 9·2% were obtained by the same method as had always given reproducible results with sulphars-phenamines. The trisodium salt derived from it also showed a similar behaviour; *e.g.*, the total sulphur found by distillation had the approximately constant values 13·2, 13·1, 13·4, and 13·3 after successive crystallisations of the trisodium salt from aqueous methyl alcohol, but the Elvove figures were respectively 9·6, 6·7, 8·3, 9·3. A search was made for the factors or conditions which might produce extreme values, but without success. The action may be an uncontrollable catalytic effect or may be connected with the complex mechanism involved in the action of alkaline iodine on dimethylenesulphites.

Observations on the Mechanism of the Elvove Reaction.—A sample of sulpharsphenamine (B), analysed in duplicate by the Elvove method, gave the values (I) S, 2·15%; (II) S, 2·2% out of a total sulphur content of 14·0%. To the filtrates 3*N*-hydrochloric acid (10 c.c.) was added in each case. In addition, to filtrate (I), 0·1032 g. of fresh sulpharsphenamine was added. Both solutions were then boiled and within 10 minutes there was a marked appearance of barium sulphate in (I). The boiling was continued for 30 minutes, during which there was no visible appearance of a precipitate in (II). At this stage the barium sulphate in (I) was removed and weighed; it corresponded to 65% of the sulphur of the second amount of sulpharsphenamine added. The liquor (II), after being boiled for 2 hours to a small volume, was filtered; the extra barium sulphate now present represented S, 5·6%. These results show that the sulphur not found by Elvove's method cannot be present as unoxidised methylenesulphite groups, since they would be readily oxidised in the acid oxidising solution. The results are, however, consistent with the view that during the alkaline iodine oxidation dithionate is formed, which is slowly transformed in the boiling acid solution with deposition of barium sulphate. A pure specimen of barium dithionate on treatment by Elvove's method showed no formation of barium sulphate and on digestion with mineral acid slowly generated barium sulphate in the same way as the sulpharsphenamine solutions under parallel conditions.

Since it has been shown that a sulpharsphenamine exposed to the quantity of alkali used in the Elvove method for 16 hours but without the iodine gives up practically all its sulphur as sulphate on completion of the Elvove conditions, it seems to follow that the action of alkaline iodine on an *NN*-dimethylenesulphite is partly hydrolytic. Any sulphite liberated by hydrolysis is, however, straightway exclusively oxidised to sulphate. At the same time there is a direct attack of the alkaline iodine on the intact dimethylenesulphite leading to oxidative union of the sulphur atoms, followed by hydrolysis and appearance of the sulphur as dithionate.

Analytical Examination of the Reaction between Aniline Hydrochlorides and Formaldehyde, followed by Sodium Hydrogen Sulphite.—The experimental conditions laid down by Newbery and Phillips were followed as closely as possible. The aniline (0·002 g.-mol.) was dissolved in N-hydrochloric acid (2 c.c., 1 equiv.), and the solution made up to 5 c.c. with water. 4% Formalin (3 c.c., 2 equivs.) was added, and after 1 minute a freshly prepared solution of sodium hydrogen sulphite (2 equivs.) prepared from anhydrous sodium carbonate (0·212 g.) in water (4 c.c.) by saturation with sulphur dioxide. By this means errors due to sulphate which is always present in commercial sodium hydrogen sulphite are avoided. The amount of free sulphur dioxide is a variable factor, but it has been controlled and shown to be immaterial by results obtained with a pure sample of sodium hydrogen sulphite. For di-acid bases the quantities of hydrochloric acid, formaldehyde, and sodium hydrogen sulphite were doubled. After 30 minutes the solution was made up to 200 c.c., and aliquot parts taken for the following analyses.

Nitrogen determinations were carried out in duplicate by the Kjeldahl method on 50 c.c. of the solution. Elvove sulphur : 25 C.c. of the solution were treated with 50 c.c. of 0·1N-iodine, followed by 20 c.c. of N-sodium hydroxide. After 1 hour the solution was acidified with 21 c.c. of N-hydrochloric acid, excess of iodine removed by addition of sufficient 0·05M-sodium arsenite, a further 5 c.c. of N-acid added, and the sulphate precipitated as barium sulphate in the usual manner. A duplicate analysis was carried out in which the iodine and sodium hydroxide were added in the reverse order. In all cases the results by both procedures were almost identical and mean values have been used in the table. Volatile sulphur : This was determined on 25 c.c. of the solution by our previously described method. For clarity, atomic ratios only are given in the following table.

Substance.	Equiv. CH₂O and NaHSO₃.	N	:	Volatile S	:	Elvove S	:	Unoxidised S
Aniline	2*	1	:	2·2	:	1·5	:	0·7
	2*†	1	:	2·0	:	1·1	:	0·9
	4	1	:	3·4	:	2·6	:	0·8
2-Aminophenol	2*	1	:	2·4	:	1·3	:	1·1
	4	1	:	4·1	:	2·8	:	1·3
4-Aminophenol	2*	1	:	2·5	:	1·9	:	0·6
2-Anisidine	2	1	:	1·7	:	1·3	:	0·4
	2*	1	:	2·5	:	1·9	:	0·6
	2*	1	:	1·7	:	1·3	:	0·4
	4	1	:	3·6	:	2·9	:	0·7
4-Amino-2-hydroxyphenylarsonic acid	2*	1	:	1·8	:	1·7	:	0·1
3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene	4*	1	:	1·9	:	1·1	:	0·8
	6*	1	:	3·3	:	2·0	:	1·3
	8*	1	:	4·4	:	3·0	:	1·4

* The concentrations are exactly the same as those of Newbery and Phillips. In all other cases the concentration is greater.

† In this case freshly prepared pure solid sodium hydrogen sulphite was used.

A control on the reliability of the results was obtained by mixing the reagents in correct amount and order without using any aniline. The weights of barium sulphate found in 25 c.c. portions of the solution were (Elvove) 0·1530 g., 0·1535 g., and (volatile) 0·1504 g.

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184. *Experiments on the Synthesis of Bergapten and its Derivatives. Part I. Furocoumarins.*

By JNANENDRA N. RÂY, SANTOKH S. SILOOJA, and VIDYA R. VAID.

BERGAPTEN has been formulated as a linear furocoumarin derivative. Karrer (*Helv. Chim. Acta*, 1920, **3**, 541) attempted the synthesis of furocoumarin from hydroxycoumarone-acrylic acid, but could not close the ring. This was obviously due to the *trans*-configuration of his acid. It has now been found that 7-hydroxycoumarin condenses with chloro-acetone and ω-bromoacetophenone in alkaline solution and the resulting *acetonyl* and

phenacyl derivatives are readily cyclised to furocoumarins by sodium ethoxide, since the intermediate hydroxycoumaroneacrylic acids have the *cis*-configuration.

Limaye (*Ber.*, 1932, **65**, 375) has prepared the angular furocoumarin (III), m. p. 176°, from the ketone (I) obtained by the Fries migration of 7-acetoxy-β-methylumbelliferone, by condensation with chloroacetic acid, subsequent ring closure with acetic anhydride, and decarboxylation. We have found that β-methylumbelliferone on condensation with chloroacetone gives a product (II), which is easily cyclised to a furocoumarin, m. p. 220°; we incline to the view that it has the linear structure (IV). Its degradation to 4 : 6-dihydroxy-*iso*phthalic acid was not successful owing to the small amount of material available, but the similar product from 7-hydroxycoumarin has been transformed into the related *trans*-coumarilic acid (the 5-hydroxy-2-methylcoumarone-4-acrylic acid of Karrer). Therefore there is no doubt as to the linear configuration of the furocoumarins described in the present paper.
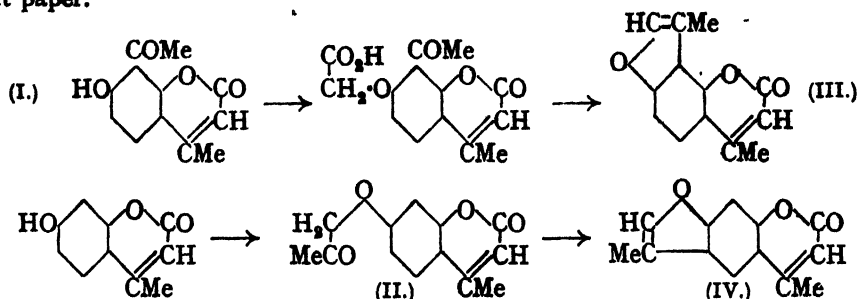
Späth and Pailer (*Ber.*, 1934, **67**, 1212), condensing sodioumbelliferone with bromo-acetal in xylene at 175—180°, obtained umbelliferone ethyl ether along with angelicin—an angular furocoumarin. In view of our results it cannot be definitely taken that in this reaction an angular condensation always occurs. However, there is some uncertainty as to the structure of our product (V), as we obtained a small quantity of a second substance in its preparation. The main product of the reaction was converted into the *oxime* and transformed by the reactions indicated below into daphnetin (m. p. and mixed m. p.).
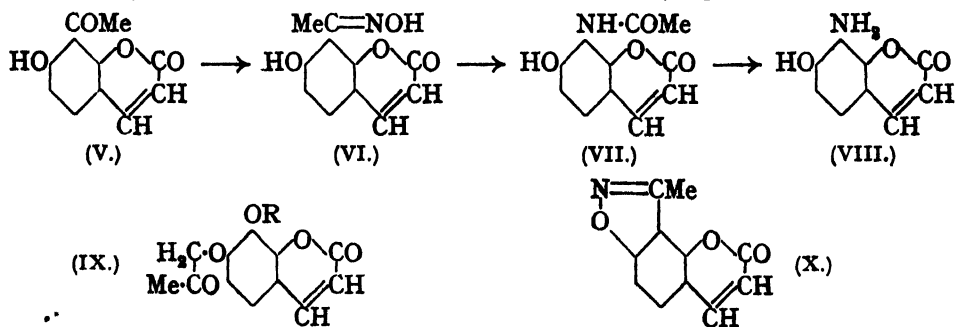
The *iso*oxazole (X) was formed along with (VII) in the Beckmann transformation; their separation was effected by means of cold dilute alkali solution.

The sodium salt of (V) does not condense with chloroacetone or chloroacetal under ordinary conditions. Therefore the smooth formation of the chloroacetic acid condensation product from (I) observed by Limaye is difficult to understand. However, we are engaged in finding the conditions for condensing (V) with chloroacetal, so that, after formation of the furocoumarin, the replacement of the acylamido-group by hydroxyl may be effected.

Daphnetin condensed with chloroacetone in presence of one molecular equivalent of alkali to give a homogeneous product, formulated as (IX; R = H), which was methylated to (IX; R = Me); this gave a furocoumarin only with difficulty. The justification for the structure (IX) is that the product is homogeneous and is dehydrated to a furocoumarin, the isomeric substance being incapable of dehydration.

EXPERIMENTAL.

Condensation of 7-Hydroxycoumarin with ω-Bromoacetophenone and with Chloroacetone.—A mixture of umbelliferone (3 g.) and alcoholic sodium ethoxide (0·55 g. of sodium) was mixed with bromoacetophenone (4·7 g.) in alcohol (10 c.c.) and was refluxed for 2½ hours after the addition of a further 15 c.c. of alcohol. The removal of the solvent left a solid, which was washed with dilute aqueous ammonia and crystallised from hot alcohol; m. p. 167° (Found : C, 72·9; H, 4·7. $C_{17}H_{12}O_4$ requires C, 72·9; H, 4·3%).

A solution of the foregoing 7-*phenacyloxycoumarin* in alcohol was treated with sodium ethoxide (1 mol.) and kept at 60° for some time. On removal of the solvent and acidification, 3'-*phenyl-7* : 6-*furocoumarin*, m. p. 200°, was obtained; it was crystallised from hot alcohol (Found : C, 77·8; H, 3·9. $C_{17}H_{10}O_3$ requires C, 77·9; H, 3·8%). It often accompanies the substance, m. p. 167°, in the preparation of the latter.

Similarly, 7-hydroxycoumarin (3 g.), dissolved in alcohol (25 c.c.), was treated with a solution of sodium (0·45 g.) in alcohol, and the mixture refluxed with chloroacetone (2 c.c.) for 2 hours. The residue after the removal of solvent was treated with dilute aqueous ammonia, and the product crystallised from alcohol; m. p. 167° (Found : C, 65·9; H, 4·3. $C_{12}H_{10}O_4$ requires C, 66·1; H, 4·6%).

The foregoing 7-*acetonyloxycoumarin* (2 g.) in pure absolute alcohol (10 c.c.) was treated with sodium ethoxide (1 mol.) for 1 hour at 60°, and the product worked up as before; 3'-*methyl-7* : 6-*furocoumarin* had m. p. 188° after crystallisation from alcohol (Found : C, 72·2; H, 3·7. $C_{12}H_8O_3$ requires C, 72·0; H, 4·0%).

A solution of this furocoumarin in hot aqueous potassium hydroxide (2 mols.) was concentrated to small bulk and exposed to ultra-violet light from a mercury vapour lamp for ½ hour. Dilute hydrochloric acid then precipitated a mixture of the coumarin and 5-hydroxy-2-methylcoumarone-4-acrylic acid, which were separated by means of dilute sodium bicarbonate solution. The acid had m. p. 199—200° after crystallisation from benzene, dissolved to a yellowish solution in sodium carbonate solution, and gave an intense bluish-violet colour with ferric chloride (Found : C, 59·9; H, 4·6. Calc. for $C_{12}H_{10}O_4$: C, 66·1; H, 4·6%).

Condensation of β-Methylumbelliferone and Chloroacetone.—β-Methylumbelliferone (3 g.), dissolved in alcohol (35 c.c.), was treated with sodium (0·4 g.) dissolved in alcohol (5 c.c.), and the resulting solution heated with chloroacetone (2 c.c.) on the steam-bath for 2 hours. 7-*Acetonyloxy-4-methylcoumarin* (II), isolated as before, had m. p. 157° after crystallisation from dilute alcohol (Found : C, 67·3; H, 5·0. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2%). It (5 g.) was treated in hot absolute alcohol (15 c.c.) with 1% alcoholic sodium ethoxide (5 c.c.), then cooled to 30—35°, and occasionally warmed during the next ½ hour. After acidification, the resulting 4 : 3'-*dimethyl-7* : 6-*furocoumarin* (IV) was dried at 100—105° and crystallised from hot 75% alcohol; m. p. 220° (Found : C, 72·6; H, 4·5. $C_{13}H_{10}O_3$ requires C, 72·9; H, 4·6%).

7-*Hydroxy-8-acetylcoumarin* (V).—Acetylumbelliferone, m. p. 147° (4·8 g.), was powdered with aluminium chloride (11 g.), and heated for 10 minutes at 130°, 15 minutes at 135°, 15 minutes at 135—140°, and 20 minutes at 140—145°. The product was decomposed with ice and the substance was collected, boiled with 20 c.c. of water, and dissolved in a boiling mixture of alcohol (25 c.c.) and water (15 c.c.) with charcoal; 7-*hydroxy-8-acetylcoumarin*, m. p. 167°, crystallised from the filtered solution (Found : C, 64·6; H, 3·6. $C_{11}H_8O_4$ requires C, 64·7; H, 3·9%); yield, 2 g.

The *oxime* (VI) had m. p. 223° after crystallisation from alcohol (Found : N, 6·6. $C_{11}H_9O_4N$ requires N, 6·4%). It (2 g.) was dissolved in phosphoryl chloride (20 c.c.) and occasionally warmed during ½ hour; the solution was then poured on ice. Treatment with alkali separated the product into two substances. The alkali-insoluble *isooxazole* (X), crystallised from dilute alcohol, had m. p. 247° (Found : N, 6·9. Calc. : N, 6·9%). 8-*Acetamido-7-hydroxycoumarin* (VII), isolated from the alkaline solution, had m. p. 251° after crystallisation from hot dilute alcohol (Found : N, 6·6. $C_{11}H_9O_4N$ requires N, 6·4%). The substance after hydrolysis with dilute acid showed a diazo-reaction indicating that it is not the methylamide of 7-hydroxycoumarin-8-carboxylic acid.

The foregoing substance (1 g.) was boiled with hydrochloric acid (*d* 1·14, 25 c.c.) and water (15 c.c.) for 3 hours. The *amine* (VIII) crystallised from dilute alcohol in fine yellow needles, m. p. 278° (Found : N, 7·9. $C_9H_7O_3N$ requires N, 7·9%). After diazotisation and decomposition it furnished a small amount of a substance having the characteristic properties of daphnetin (m. p. and mixed m. p.).

Daphnetin-3-carboxylic Acid.—A mixture of pyrogallaldehyde (1·5 g.), malonic acid (3 g.),

pyridine (10 c.c.), and a drop of piperidine was heated on the steam-bath for 1 hour and over a free flame for 2 minutes. The mixture was diluted with water (20 c.c.) and acidified. The pale greenish-yellow substance obtained, recrystallised from hot dilute acetone, gave *daphnetin-3-carboxylic acid*, m. p. 228° (Found : C, 54·3; H, 2·6. $C_{10}H_6O_6$ requires C, 54·0; H, 2·7%).

The preparation of daphnetin from pyrogallol and malic acid was advantageous from the point of view of yield but not of purity.

Condensation of Daphnetin and Chloroacetone.—Daphnetin (1·0 g.) was dissolved in alcohol (10 c.c.), treated with sodium ethoxide solution (0·13 g. of sodium), mixed with a solution of chloroacetone (0·5 g.) in alcohol, and heated for 3 hours on the steam-bath. After removal of the solvent, water precipitated 8-*hydroxy*-7-*acetonyloxycoumarin* (IX, R = H), which was crystallised from hot benzene; m. p. 132—133°. It was soluble in dilute alkali solution (Found : C, 61·5; H, 4·4. $C_{12}H_{10}O_5$ required C, 61·5; H, 4·3%).

The foregoing substance (0·5 g.) was dissolved in alcohol (10 c.c.) by heating, cooled, mixed with a solution of 0·05 g. of sodium in alcohol, and shaken with methyl sulphate (0·35 g.) for ½ hour. After warming on the steam-bath for ¼ hour, the solvent was removed, water added, and the mixture extracted with benzene. The extract was freed from alkali-soluble substances and evaporated; the resulting crystalline material, recrystallised from boiling benzene–ligroin, formed silky needles, m. p. 81—82°, of 8-*methoxy*-7-*acetonyloxycoumarin* (Found : C, 62·65; H, 5·3. $C_{13}H_{12}O_5$ requires C, 62·9; H, 4·8%). This substance (0·2 g.) was dissolved in alcohol (8 c.c.) and kept with sodium ethoxide solution (1 mol.) at 70° for 2 hours. After removal of alcohol, water (4 c.c.) was added; the precipitated 8-*methoxy*-3′-*methyl*-7 : 6-*furocoumarin* crystallised from hot dilute alcohol in very pale yellow needles, m. p. 155° [Found (microanalysis by Dr. Weiler) after drying at 90° : C, 63·2; H, 5·2. $C_{13}H_{10}O_4,H_2O$ requires C, 62·9; H, 4·8%], insoluble in alkali solution.

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185. *Substituted Aromatic Aldehydes in Hantzsch's Pyridine Condensation. Part IV. Derivatives of* 3 : 4-*Dihydroxybenzaldehyde.*

By L. E. HINKEL, E. E. AYLING, and W. H. MORGAN.

IN order to extend the study of the effect of the nitro-group on the behaviour of aromatic aldehydes in Hantzsch's pyridine synthesis, the condensation of the methyl ethers of 3 : 4-dihydroxybenzaldehyde, namely, vanillin, *iso*vanillin, and veratraldehyde, and of six of their nitro-derivatives has been investigated.

Vanillin, *iso*vanillin, and veratraldehyde exhibit very little difference in behaviour, the yields, 74, 73, and 76% respectively, approximating to those given by benzaldehyde and *m*-methoxybenzaldehyde (74 and 75% respectively; see Part II, J., 1931, 1835).

The effect of a nitro-group in these methyl ethers is markedly less than has been observed in previous cases, but the nitro-groups in 5-nitro*iso*vanillin (76% yield) and 6-nitro-veratr-aldehyde (68%) tend to influence the condensation in the normal manner, the *m*- and *o*-nitro-groups having an effect analogous to, but less than, that of these groups in similar positions in benzaldehyde (*loc. cit.*). As previously observed with 2 : 6-dinitro-3-methoxy-benzaldehyde (Part III, J., 1932, 1112), the presence of two *o*-nitro-groups in 2 : 6-dinitro-*iso*vanillin inhibits the condensation. An unexpected result with this compound was the formation of its ammonium salt, which also failed to react in the condensation.

With three substituents present, the likelihood for anomalies, due to the mutual influence of substituents, is increased and the nitro-groups in 5-nitro- and 2-nitro-veratraldehyde and 2-nitrovanillin yield anomalous results, the *m*-nitro-group in the first causing a diminution in yield (76 to 70%) and the *o*-nitro-group in the second having no appreciable effect. With 2-nitrovanillin, consistent yields could not be obtained, but the highest recorded (72%) indicates that the *o*-nitro-group is having only a slight influence.

Four other derivatives of 3 : 4-dihydroxybenzaldehyde examined were the methylene ether, piperonal, and its 6-bromo-, 6-chloro-, and 6-nitro-derivatives, which give yields of 72, 70, 67, and 61% respectively. Piperonal thus compares with the above methyl ethers, the *o*-substituent decreasing the yield in each case.

The diminutions with the chloro- and nitro-compounds (5 and 11%) compare with those caused by chlorine and the nitro-group in the *o*-position in benzaldehyde (12%, Part II). The order of influence on the yield is : Br<Cl<NO$_2$, which corresponds to the normal sequence of increase of general inductive effect with these three substituents, thus indicating that the ortho-effect of the substituent is polar rather than steric. In the latter event, the substituents would be placed in the order : Cl<NO$_2$<Br, taking, as a measure of the spatial effect, the " internuclear distances " calculated by Stanley and Adams (*J. Amer. Chem. Soc.*, 1930, **52**, 1200; compare Adams and Yuan, *Chemical Reviews*, 1933, **12**, 284) for determining the possible interference of groups in the 2 : 2′ : 6 : 6′-positions in diphenyl.

Shaw and Wagstaffe (J., 1933, 77) consider that the influence of a nitro-group on the behaviour of an aromatic aldehyde should only be an enhancing one, giving the order : 2 : 4-dinitro>mononitro>unsubstituted, in accordance with their observations on the condensation of aromatic aldehydes with 2-picoline and with those of Bennett and Willis (J., 1928, 1960) on condensations with 2-methylquinoxaline. We have examined, in all, the behaviour of seventeen mono- and four di-nitro-aldehydes in the Hantzsch condensation, and in only seven cases is the yield with the nitro-aldehyde greater than with the corresponding unsubstituted aldehyde; these seven nitro-aldehydes all contain *m*-nitro- or *mm′*-dinitro-groups. With each of the seven *o*-nitro- and three *p*-nitro-aldehydes studied, the yield is never greater than with the corresponding unsubstituted aldehyde, the diminutions in yield generally approximating to those observed with benzaldehyde itself, and *oo′*-dinitro-groups appear completely to inhibit the condensation. Where comparisons are possible, the relations originally derived for the enhancing influence of a nitro-group, *viz.*, *m*>unsubstituted and *m*->*o*- and *p*- (compare Part II), are usually confirmed.

<center>EXPERIMENTAL.</center>

Materials.—The substituted aldehydes employed were prepared in accordance with the authorities cited : veratraldehyde (Perkin and Robinson, J., 1907, **91**, 1079), 2-nitrovanillin, 2-nitro- and 6-nitro-veratraldehydes (Pschorr and Sumuleanu, *Ber.*, 1899, **32**, 3407; compare Pisovschi, *Ber.*, 1910, **43**, 2139), 5-nitro*iso*vanillin, 5-nitroveratraldehyde, and 2 : 6-dinitro*iso*vanillin (Pschorr and Stöhrer, *Ber.*, 1902, **35**, 4393); 6-nitro- (Parijs, *Rec. trav. chim.*, 1930, **49**, 18; compare Wilkendorf, *Ber.*, 1919, **52**, 606), 6-chloro- and 6-bromo-piperonal (Parijs, *loc. cit.*; Orr, Robinson, and Williams, J., 1917, **111**, 947). The 5-nitro*iso*vanillin obtained melted at 121° (recorded m. p. 113°) (Found : C, 48·8; H, 3·7. Calc. : C, 48·7; H, 3·6%).

Standard Method of Condensation.—The procedure previously described (J., 1931, 1839) was adopted throughout. With each aldehyde the condensation was carried out in duplicate, the mean of the two yields being the value recorded in the introductory portion.

Condensations with Vanillin and 2-Nitrovanillin.—Ethyl 4-(4′-*hydroxy-3′-methoxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* crystallised from alcohol in colourless needles, m. p. 164° (Found : C, 64·4; H, 6·8. C$_{20}$H$_{25}$O$_5$N requires C, 64·0; H, 6·7%). Yields : 13·9 and 13·9 g., 74·1%. Methylation of this compound with methyl sulphate and sodium hydroxide yielded the dimethoxy-derivative, m. p. 144°, identical with the dihydropyridine derivative obtained from veratraldehyde (see below).

Ethyl 4-(2′-*nitro-4′-hydroxy-3′-methoxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* crystallised from ethyl acetate in light yellow plates, m. p. 118° (Found : C, 56·7; H, 5·8. C$_{20}$H$_{24}$O$_7$N$_2$ requires C, 57·1; H, 5·7%). It was not possible to obtain consistent yields in the condensation, owing to the difficulty of isolating the product free from sticky material without loss. The compound was best isolated by complete evaporation of the alcohol from the reaction mixture, dissolution of the sticky residue in ether, and washing of the ethereal solution with dilute sulphuric acid. The product obtained on removal of ether from the dried ethereal solution was recrystallised as above. Examples of yields : 15·1 and 12·1 g., 71·9 and 57·6%.

Condensations with isoVanillin and 5-Nitroisovanillin.—*Ethyl* 4-(3′-*hydroxy-4′-methoxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* crystallised from aqueous alcohol in light yellow needles, m. p. 165° (Found : C, 64·4; H, 6·8. C$_{20}$H$_{25}$O$_5$N requires C, 64·0; H, 6·7%). Yields : 13·9 and 13·65 g., 74·1 and 72·8%. Methylation of the compound, as above, yielded the dimethoxy-derivative, identical with the dihydropyridine derivative obtained from veratraldehyde (see below).

Ethyl 4-(5'-*nitro*-3'-*hydroxy*-4'-*methoxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarb-oxylate* crystallised from alcohol in orange-yellow prismatic needles, m. p. 185°, containing alcohol of crystallisation (Found : C, 56·2; H, 6·3; C_2H_5·OH, 9·9. $C_{20}H_{24}O_8N_2,C_2H_5$·OH requires C, 56·7; H, 6·4; C_2H_5·OH, 9·9%), which, on being heated at 110—120° for 2 hours, yielded the alcohol-free *compound* as a light yellow powder, m. p. 185° (Found : C, 57·1; H, 5·2; N, 7·1. $C_{20}H_{24}O_8N_2$ requires C, 57·1; H, 5·7; N, 6·7%). Yields (of alcohol-free product) : 15·9 and 15·9 g., 75·7%.

Condensations with Veratraldehyde and its Nitro-derivatives.—*Ethyl* 4-(3' : 4'-*dimethoxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* crystallised from alcohol in colourless prisms, m. p. 144° (Found : C, 64·7; H, 7·0. $C_{21}H_{27}O_6N$ requires C, 64·8; H, 6·9%). Yields : 14·8 and 14·9 g., 76·1 and 76·6%.

Ethyl 4-(2'-*nitro*-3' : 4'-*dimethoxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* crystallised from alcohol in colourless plates, m. p. 141·5° (Found : C, 57·6; H, 6·1; N, 6·8. $C_{21}H_{26}O_8N_2$ requires C, 58·1; H, 6·0; N, 6·5%). Yields : 16·1 and 16·7 g., 74·2 and 77·0%.

Ethyl 4-(5'-*nitro*-3' : 4'-*dimethoxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* crystallised from alcohol in light yellow needles, m. p. 154° (Found : C,,57·6; H, 6·1%). Yields : 15·05 and 15·5 g., 69·3 and 71·4%.

Ethyl 4-(6'-*nitro*-3' : 4'-*dimethoxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* crystallised from alcohol in yellow prisms, m. p. 229° (Found : C, 58·3; H,.6·1%). Yields : 14·9 and 14·6 g., 68·7 and 67·3%.

Condensations with 2 : 6-*Dinitro*isovanillin *and its Ammonium Salt.*—Condensation of 2 : 6-dinitroisovanillin yielded only the *ammonium* salt of the nitro-aldehyde, which crystallised from methyl alcohol–acetone in fine reddish needles, m. p. 190° (decomp.) (Found : C, 36·7; H, 3·6. $C_8H_9O_7N_3$ requires C, 37·1; H, 3·5%). The salt, when shaken with warm dilute hydrochloric acid, regenerated the original nitroaldehyde. Condensation of the ammonium salt was attempted, but it was recovered unchanged.

Condensations with Piperonal and its Derivatives.—*Ethyl* 4-(3' : 4'-*methylenedioxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* crystallised from methyl alcohol in pale yellow prisms, m. p. 132° (Found : C, 64·2; H, 6·4. $C_{20}H_{23}O_6N$ requires C, 64·3; H, 6·2%). Yields : 13·4 and 13·3 g., 71·9 and 71·3%.

Ethyl 4-(6'-*chloro*-3' : 4'-*methylenedioxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarb-oxylate* crystallised from methyl alcohol in pale yellow prisms, m. p. 139° (Found : Cl, 8·3. $C_{20}H_{22}O_6NCl$ requires Cl, 8·7%). Yields : 13·6 and 13·7 g., 66·7 and 67·2%.

Ethyl 4-(6'-*bromo*-3' : 4'-*methylenedioxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarb-oxylate* separated from methyl alcohol as a yellow crystalline mass, m. p. 169° (Found : Br, 17·8. $C_{20}H_{22}O_6NBr$ requires Br, 17·7%). Yields : 15·8 and 15·7 g., 69·9 and 69·5%.

Ethyl 4-(6'-*nitro*-3' : 4'-*methylenedioxyphenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarb-oxylate* crystallised from glacial acetic acid in yellow plates, containing solvent of crystallisation, m. p. 144° (Found : C, 55·7; H, 5·0; N, 6·1. $C_{20}H_{22}O_8N_2,C_2H_4O_2$ requires C, 55·2; H, 5·4; N, 5·9%), and from alcohol in pale yellow plates, with solvent of crystallisation, m. p. 101° (decomp.) (Found : C, 56·4; H, 6·1. $C_{20}H_{22}O_8N_2,C_2H_6O$ requires C, 56·9; H, 6·0%). Yields (as solvent-free material) : 12·45 and 12·85 g., 59·6 and 61·5%.

186. *Compounds of α-Benzoinoxime with Bivalent Metals.*

By J. S. JENNINGS, E. SHARRATT, and W. WARDLAW.

BENZOINOXIME is one of a number of organic reagents recently employed in the detection and estimation of metals. The copper derivative, discovered by Feigl (*Ber.*, 1923, **56**, 2083), is a deep green, amorphous compound which is insoluble in water and organic solvents and when dried at 105—115° contains 22·02% Cu in accordance with the formula (I) assigned to it by Feigl. This structure, however, cannot be regarded as fully established.

It is unusual to find the hydrogen atom of the secondary alcoholic group replaced by

copper; moreover, benzoinoxime is a reducing agent and one would expect it to reduce a proportion of the cupric salt to the cuprous state. From the analytical data, structure
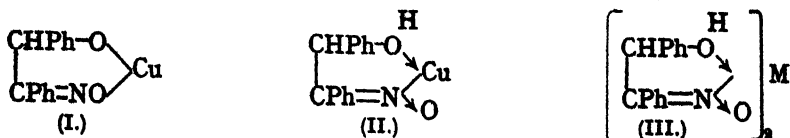
(II), which is that of a cuprous compound, is a possible alternative to (I). Decomposition of Feigl's compound with hydrochloric acid yielded cuprous chloride, but, as hydroxylamine hydrochloride was formed simultaneously, this is no indication of the valency state of the copper. Convincing evidence in favour of (I) has, however, been obtained by treating Feigl's compound with alcoholic hydrogen chloride; the green crystalline salt (IIa) then separates with a molecule of alcohol of crystallisation. With hot water, two molecules of hydrogen chloride are eliminated from (IIa) and the original compound (I) is produced. A compound of formula (II) would give the derivative (IIb) on treatment with
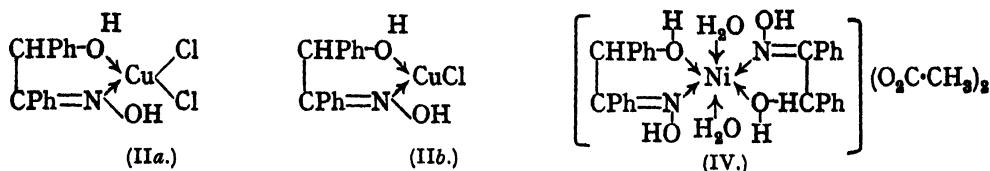
alcoholic hydrogen chloride. Whilst Feigl's compound must have structure (I), there is, at present, no decisive evidence whether the ring is five- or six-membered.

Feigl states that nickel and cobalt salts do not give precipitates with benzoinoxime, but it is mentioned in " Organic Reagents for Metals " (1934, p. 19) that this is incorrect. We agree with the latter opinion, for we find that these metals give respectively a brown and a buff precipitate with the reagent. In addition, bivalent palladium and platinum give derivatives with benzoinoxime; the former immediately, and the latter slowly. Considerable difficulty was experienced in preparing any of these compounds pure, owing to the coprecipitation of the benzoinoxime, which is difficultly soluble in aqueous alcohol. However, pure products were obtained in all cases except that of cobalt, and these were covalent compounds of the type (III), where M = Ni, Pd, Pt. In no case, by varying the experimental conditions, could we obtain a derivative similar to that of copper.

We have also been able to show in the case of nickel that the oxime can function as a chelate group attached by two co-ordinate links. We find that, when an alcoholic solution of benzoinoxime reacts with aqueous nickel sulphate in presence of large concentrations of ammonium acetate or excess of sodium acetate and acetic acid, the usual brown precipitate of *nickel dibenzoinoxime* is first produced, but on standing at 40° for an hour, the substance changes to a brilliant green complex *salt*. It is sparingly soluble in hot water, and with dilute sulphuric acid yields acetic acid. The water of crystallisation is not removed from it on drying for 12 hours in a desiccator over phosphoric oxide. It appears to have the structure (IV), and when it is warmed with ammonia, alcohol, or acetone, the brown nickel compound of type (III) is produced.

It will be seen the α-benzoinoxime may function as a chelate group in three ways. In Feigl's formula (I), it may be attached to a copper atom by two principal valencies. With other bivalent metals it may be associated by either one principal valency and one co-ordinate link, as in (III), or by two co-ordinate links, as in (IV) and (IIa).

The nickel compound (III) is a buff-coloured substance, which dissolves very readily in benzene, chloroform, acetone, and carbon tetrachloride, brown solutions being produced. If the solution in the last solvent is kept in the cold for about 10 minutes, minute crystals separate, the process continuing for 2—3 days. After 12 hours, however, little of the substance remains in solution, the *product* consisting of orange-coloured crystals, $[(C_{14}H_{12}O_2N)_2Ni],CCl_4$. On standing in air for a few days, or on heating at 90° for 4—5 hours, the solvent of crystallisation is lost, and the colour of the material changes to reddish-

brown. This second variety of nickel dibenzoinoxime is almost completely insoluble in all organic solvents except chloroform; evaporation of the chloroform solution gives the first variety. Thus the two forms of nickel dibenzoinoxime are interconvertible:

$$\text{First variety} \underset{\text{CHCl}_4}{\overset{\text{CCl}_4}{\rightleftharpoons}} \text{second variety.}$$
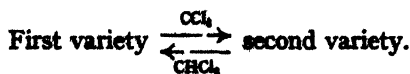
Alcohol and acetone convert the first of the nickel compounds into the second variety, but the process is always accompanied by decomposition. When either variety is treated with alcohol or acetone at 40°, benzoinoxime is liberated. Benzene and ether behave similarly to carbon tetrachloride, but are less suitable for producing the second modification, the former on account of the much slower rate of the change, and the latter on account of its volatility. Phenol does not cause any change in either material below 75°, but there is a partial conversion of the second form into the first form above this temperature. The molecular weight of the first variety was therefore determined cryoscopically in phenol; the results prove it to be monomeric. No means of determining the molecular weight of the second variety could be found, since in chloroform, the only solvent for it, it reverted to the first modification.

The first *platinum* compound of type (III) is formed when potassium chloroplatinite and the oxime are kept at 40° in aqueous alcohol for 2—3 hours. The substance is dark yellow, and resembles the nickel compound in its ready solubility in organic solvents. Moreover, it reverts to a second form in carbon tetrachloride after some days. Ethyl alcohol, however, accomplishes the conversion more speedily, but even here the process is slow in comparison with the rate of change of the nickel isomerides. The second variety of the platinum benzoinoxime is pink-brown, amorphous, and soluble only in chloroform, behaving in the same manner as the second nickel compound.

The addition of benzoinoxime to potassium chloropalladite gives, immediately, a bulky primrose-yellow precipitate of *palladium dibenzoinoxime* (III). Although soluble in most of the usual organic solvents, it has not the great solubility of its nickel and platinum analogues, and it gives yellow solutions instead of the brown solutions always produced by the derivatives of these metals. In acetone, alcohol, benzene, and carbon tetrachloride, it reverts to a second variety, which has a slightly deeper yellow colour and is almost insoluble in all the usual organic reagents.

The molecular weight of the first palladium compound in phenol was determined, as was also that of the first platinum complex in chloroform; both proved to be unimolecular.

Thus, nickel, platinum, and palladium dibenzoinoximes each exist in two forms. Their m. p.'s varied with the rate of heating, owing to slow decomposition occurring before the true m. p.'s were reached. This was particularly noticeable with the first platinum benzoinoxime, which became bright red at 132°, and after being kept at this temperature for some minutes, melted at 140°, whereas the m. p. recorded in the usual way was 150—155°. Similar fluctuations were observed in the m. p.'s of the nickel and palladium derivatives.

We have no satisfactory explanation why two nickel derivatives of α-benzoinoxime exist. Professor S. Sugden very kindly examined these substances for us, and found them to be paramagnetic. This is against the idea that they have a planar configuration. On the other hand, the palladium derivatives were diamagnetic, so that the possibility that they have a planar configuration is not excluded. The two modifications in the three cases may arise from purely optical isomerism. α-Benzoinoxime is a *dl*-mixture, and when a complex compound is made with two benzoinoxime residues, there is the possibility that it may be a *meso*- or a racemic *dl*-modification. Against this view, however, is the experimental evidence that the two modifications are never present in the original preparations, and it seems most unlikely that dissolution in carbon tetrachloride would change a *meso*-form into a *dl*-mixture, or *vice versa*. Both varieties of the metallic derivatives give α-benzoinoxime when treated with cold dilute hydrochloric acid ($N/2$). The last possibility is that one form is a polymeride of the other; as the metal atoms in each case have the expected covalency of four, this does not appear probable.

Copper Benzoinoxime.—An aqueous solution of cupric chloride (1·5 g.; 200 c.c.) was mixed with an alcoholic solution of α-benzoinoxime (2 g.; 100 c.c.), the mixture being rendered faintly ammoniacal by the careful addition of aqueous ammonia (3N). A dark green precipitate formed immediately. This was washed with hot 1% aqueous ammonia, alcohol, and hot water and dried at 110—115° (Found: Cu, 21·95. Calc. for $C_{14}H_{11}O_2NCu$: Cu, 22·0%).

Copper Benzoinoxime Dichloride.—Copper benzoinoxime (1 g.) was dissolved in hot alcoholic hydrogen chloride (20 c.c.). The filtered solution, on cooling, deposited bright emerald-green crystals of *copper benzoinoxime dichloride* containing one molecule of alcohol of crystallisation. These were removed, washed with alcohol (10 c.c.), and air-dried [Found: Cu, 15·56, 15·55; Cl, 17·31. $(C_{14}H_{13}O_2N)CuCl_2,C_2H_5\cdot OH$ requires Cu, 15·57; Cl, 17·38%]. After some days these crystals lost their alcohol of crystallisation. They were readily soluble in alcohol and acetone, but were decomposed by water, yielding the original green copper benzoinoxime and free hydrogen chloride.

Nickel Dibenzoinoxime.—*First form.* Nickel sulphate (2 g.; $NiSO_4.7H_2O$) and ammonium chloride (5 g.) were dissolved in water (180 c.c.). Aqueous ammonia (20 c.c.; 3N) was then added, and the mixture heated to 65—70°. α-Benzoinoxime (1 g.) dissolved in alcohol (100 c.c.) was added. A buff-coloured precipitate formed immediately, and was filtered off after 10 minutes. The product was extracted twice with 30% aqueous alcohol (200 c.c.) at 60° to remove unchanged benzoinoxime, and then washed with hot water till free from inorganic impurities. The material was dried in a desiccator over phosphoric oxide for 3 days or placed in an oven at 90° for 5 hours [Found: Ni, 11·52; N, 5·37. $(C_{14}H_{12}O_2N)_2Ni$ requires Ni, 11·49; N, 5·48%].

In this preparation, concentrations of alcohol greater than 35% must be avoided, since this may cause some decomposition or effect a partial transformation to the second variety, whilst with low concentrations of alcohol much benzoinoxime is always precipitated, particularly at low temperatures. Analysis of the product is best effected by warming with N-hydrochloric acid, the precipitated oxime being filtered off, and the nickel estimated as the dimethylglyoxime compound. Complete decomposition of the substance with concentrated nitric acid causes the formation of benzaldehyde·which is most undesirable.

Second form. The first variety (1 g.) was dissolved in carbon tetrachloride (40 c.c), an intense brown colour being produced. The solution was filtered as rapidly as possible. After 10 minutes' standing, the formation of a precipitate began and continued for 2 or 3 days. At the end of the first day, the orange-coloured crystalline product was removed. Analysis showed that it contained one molecule of carbon tetrachloride of crystallisation [Found : Ni, 8·82, 8·88. $Ni(C_{14}H_{12}O_2N)_2,CCl_4$ requires Ni, 8·83%]. This was removed by 5 hours' heating at 90°, the colour of the substance becoming reddish-brown (Found: Ni, 11·37, 11·38; N, 5·46%).

Nickel Dibenzoinoxime Diacetate.—Nickel sulphate (12 g.; hydrated salt) and ammonium acetate (20 g.) were dissolved in water (200 c.c.) and heated to 40°. Benzoinoxime (4 g.), dissolved in alcohol (100 c.c.) and heated to 40°, was added to the aqueous solution and the mixture maintained at this temperature for 1 hour. The brown nickel dibenzoinoxime dissolved slowly, and an emerald-green precipitate formed. This was filtered off, extracted with warm 50% aqueous alcohol, washed with water, and dried in a desiccator {Found: Ni, 8·74; N, 4·43. $[Ni(C_{14}H_{13}O_2N)_2](CH_3\cdot CO_2)_2,2H_2O$ requires Ni, 8·80; N, 4·20%}.

This substance was also prepared by the following method. Nickel sulphate (2 g., hydrated salt) and sodium acetate (10 g.) were dissolved in water (200 c.c.) at 40°, and a solution of benzoinoxime (2 g.) in alcohol (100 c.c.), also at 40°, was added. Brown nickel benzoinoxime was precipitated immediately. N-Acetic acid (25 c.c.) was then added slowly with stirring. The brown precipitate dissolved rapidly, and the green *nickel dibenzoinoxime diacetate* crystallised gradually during 1½ hours. The product was removed, washed twice with 50% aqueous alcohol (100 c.c.) at 40°, and with hot water. It was then dried in a desiccator (Found: Ni, 8·78; N, 4·20%).

Palladium Dibenzoinoxime.—*First form.* To potassium chloropalladite (1·5 g.), dissolved in water (200 c.c.), an alcoholic solution of benzoinoxime (2·5 g., 100 c.c.) was added, and the mixture warmed at 60° for about 20 minutes. The very pale primrose-yellow precipitate, which formed immediately, was removed, extracted twice with 33% aqueous alcohol, washed thoroughly with hot water, and finally dried in a desiccator over phosphoric anhydride [Found: Pd, 19·10; N, 4·85. $Pd(C_{14}H_{12}O_2N)_2$ requires Pd, 19·10; N, 5·01%]. Excess of chloropalladite must

3 H

be avoided in this preparation, or the product will be contaminated with another substance of higher palladium content.

Second form. The above *palladium dibenzoinoxime* (1 g.) was dissolved in chloroform, (50 c.c.) and filtered as quickly as possible. After 10 minutes, a precipitate had formed, but the process of separation was allowed to continue for 24 hours, whereupon the pale primrose-yellow solid was removed, and dried in a desiccator. Carbon tetrachloride, acetone, or alcohol may be used instead of chloroform with equally good results (Found, in product from $CHCl_3$: Pd, 19·10; N, 5·01%).

Platinum Dibenzoinoxime.—First form. Potassium chloroplatinite (1 g.) was dissolved in water at 45°. Benzoinoxime (1 g.), dissolved in alcohol, was added to the solution, and the mixture maintained at 40—45° for 3 hours, while the *platinum dibenzoinoxime* formed slowly. This ochre-coloured material was filtered off, extracted twice with 33% alcohol (100 c.c.) at 40°, and washed with warm water. It was then dried in a desiccator with phosphoric oxide [Found : Pt, 30·12; N, 4·36. $Pt(C_{14}H_{12}O_2N)_2$ requires Pt, 30·15; N, 4·35%]. If, during this preparation, the temperature of the mixture is allowed to rise above 50°, intensely reddish-brown impurities result, and above 70°, the product melts to a separate layer which solidifies on cooling to an intensely brown mass of high platinum content. Attempts to accelerate the reaction by the addition of sodium acetate were unsuccessful; the presence of free mineral acid apparently has no effect on the reaction.

Second form. The foregoing product (1 g.) was dissolved in carbon tetrachloride (50 c.c.), filtered, and the intensely brown solution set aside. A precipitate formed very slowly, and after 3 weeks, the pink-brown deposit was removed, and dried in a desiccator. Alternatively, the first variety (1 g.) is dissolved in alcohol (100 c.c.), and the solution filtered; after 2 days, the pink-brown precipitate is removed and dried (Found, using carbon tetrachloride : Pt, 29·93; using alcohol : Pt, 30·21; N, 4·32%).

Molecular-weight Determinations.

Below are recorded the results from the molecular-weight determinations with the first forms of the metallic derivatives of α-benzoinoxime.

Cryoscopic determinations in phenol (constant = 7·27° per 1000 g.).

	Concn (g./1000 g.).	Δt.	M Found.	M Calc.
$Ni(C_{14}H_{12}O_2N)_2$	11·21	0·165°	494	511
	20·05	0·295	494	511
$Pd(C_{14}H_{12}O_2N)_2$	9·80	0·126	565	559

Ebullioscopic determinations in chloroform (constant = 2·6° per 1000 c.c.).

	(g./1000 c.c.)			
$Ni(C_{14}H_{12}O_2N)_2$	17·91	0·091	512	511
	20·71	0·105	513	511
$Pt(C_{14}H_{12}O_2N)_2$	23·29	0·095	637	647
	31·58	0·128	641	647

187.   *The Association of Water and Deuterium Oxide in Dioxan Solution.*

By R. P. BELL and J. H. WOLFENDEN.

IN comparing the physical properties of pure water and deuterium oxide, some of the differences observed (such as the change in the temperature of maximum density) can be attributed to a difference in the " degree of association " of these two liquids. It was thought of interest to investigate whether this difference persists in moderately dilute solutions of the two kinds of water. Dioxan (diethylene dioxide) is a non-polar solvent

of convenient freezing point which is miscible with water in all proportions, and is thus a suitable solvent for detecting any such differences by means of freezing-point measurements. Chlorobenzene was used as a normal solute for comparison.

The dioxan was a pure product dried over calcium chloride and sodium, and froze at 11·8°. The specimen of D_2O was kindly supplied by Professor H. S. Taylor, and contained not less than 99·8% D_2O. The chlorobenzene was dried over phosphoric oxide and fractionally distilled; the middle fraction boiling within 0·1° was used.

The measurements were carried out by means of the usual Beckmann technique,[*] about 10 g. of dioxan being used in each experiment. The freezing-point depressions in the following table represent the mean of 2—4 readings. The data for water were obtained in five independent series of measurements. In the tables, m is the concentration in molality (g.-mols. per 1000 g. of solvent), and ΔT the freezing-point depression.

TABLE I.

Solutions of H_2O in dioxan.

m.	ΔT.	$\Delta T/m$.	Deviation.	m.	ΔT.	$\Delta T/m$.	Deviation.	m.	ΔT.	$\Delta T/m$.	Deviation.
0·0955	$0·42_2$°	4·39°	$-0·00_2$°	0·456	$1·78_0$°	3·90°	$-0·05_0$°	1·042	$3·35_0$°	3·21°	$0·00_0$°
0·121	$0·52_0$	4·31	$-0·01_5$	0·575	$2·19_0$	3·82	$-0·01_0$	1·142	$3·54_5$	3·02	$-0·01_0$
0·161	$0·72_0$	4·43	$0·00_0$	0·626	$2·41_5$	3·86	$+0·05_5$	1·204	$3·60_5$	2·99	$-0·05_5$
0·244	$1·06_0$	4·37	$+0·00_0$	0·719	$2·61_5$	3·63	$0·00_0$	1·390	$3·96_5$	2·85	$0·00_5$
0·246	$1·05_5$	4·29	$-0·00_5$	0·830	$2·92_0$	3·52	$+0·01_5$	1·517	$4·18_5$	2·76	$0·00_0$
0·321	$1·33_0$	4·15	$-0·01_5$	0·840	$2·90_0$	3·46	$-0·02_5$	1·572	$4·32_5$	2·74	$+0·05_5$
0·335	$1·39_5$	4·16	$0·00_0$	0·886	$2·98_5$	3·33	$-0·05_0$	1·652	$4·39_0$	2·66	$+0·00_5$
0·336	$1·48_0$	4·40	$+0·02_0$	1·003	$3·33_0$	3·32	$+0·04_0$	1·747	$4·49_0$	2·57	$-0·04_0$

TABLE II.

Solutions of D_2O in dioxan.

m.	ΔT.	$\Delta T/m$.	Dev.	m.	ΔT.	$\Delta T/m$.	Dev.	m.	ΔT.	$\Delta T/m$.	Dev.
0·204	$0·88_0$	4·30	$-0·02_0$	1·126	$3·43_5$	3·05	$-0·09_5$	1·594	$4·21_5$	2·64	$-0·09_0$
0·617	$2·26_0$	3·66	$-0·07_5$	1·350	$3·81_0$	2·82	$-0·09_5$	1·819	$4·49_0$	2·47	$-0·14_5$
0·954	$3·09_5$	3·24	$-0·09_5$								

TABLE III.

Solutions of chlorobenzene in dioxan.

m.	ΔT.	$\Delta T/m$.	m	ΔT.	$\Delta T/m$.	m.	ΔT.	$\Delta T/m$.
0·087	$0·39_0$°	4·47°	0·508	$2·32_0$°	4·56°	0·842	$3·76_0$°	4·47°
0·193	$0·91_0$	4·72	0·609	$2·77_0$	4·55	0·916	$4·05_5$	4·43
0·399	$1·82_5$	4·56	0·761	$3·42_5$	4·51	1·040	$4·54_5$	4·37

The freezing points of the H_2O solutions were plotted against their concentrations, and a smooth curve drawn to fit the points as closely as possible. Col. 4 of Table I gives the deviations (in temperature) of the individual points from this curve, the average deviation being $\pm0·020$°. On plotting the points for D_2O on the same graph, it was found that they all lay slightly below the curve (see Table II, col. 4). With the exception of the most dilute solution of D_2O (where the association is very small), the negative deviations for D_2O range from 3 to 7 times the mean deviation for H_2O, and they are individually all greater than the greatest deviation observed for H_2O. It must thus be concluded that D_2O is slightly but unmistakably more associated than H_2O in dioxan solutions of the same molar concentration.

The figures for chlorobenzene serve to establish the molecular freezing-point depression for dioxan. [The slight decrease of the values of $\Delta T/m$ with increasing concentration is no more than would be expected for an ideal solute, owing to the fact that we are plotting against m instead of log $(1 - x)$, where x is the mole-fraction of solute.] The value 4·65 being taken for $\Delta T/m$ at infinite dilution, this gives 0·75 and 0·58 for the osmotic coefficients of H_2O at $1M$ and $2M$ respectively. The corresponding coefficients for D_2O appear to be about 3% less.

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[*] Although the Beckmann method is not suitable for accurate absolute measurements, yet under constant conditions it gives very reproducible results, and therefore lends itself to comparative measurements such as those described.

It is interesting to speculate as to the cause of this difference. The abnormal behaviour of pure hydroxyl compounds has been explained by assuming the formation of a "hydrogen bond" between two molecules (Sidgwick, *Ann. Reports*, 1934, **31**, 41). If this factor is also operative in dilute solutions, then our results indicate that the "deuterium bond" is formed more readily than the "hydrogen bond." It is noteworthy, however, that an explanation is possible on the basis of a purely electrostatic interaction between the water dipoles. Fuoss (*J. Amer. Chem. Soc.*, 1934, **56**, 1027) has derived a limiting expression for the osmotic coefficient g (in a medium of dielectric constant D) of ellipsoidal molecules with axes a and b having dipoles of moment μ at their centres. His expression is

$$1 - g = n\left(\frac{\pi}{3}\right)^{3/2}\frac{\mu^2}{2DkT}\left(\frac{2b^2}{a^2 - 2b^2}\right)^{1/2}\left(\frac{\mu^2}{b^3DkT}\right)^{7/2}e^{\mu^2/b^3DkT}$$

where n is the number of solute molecules per c.c. With $D = 2\cdot20$ and $\mu = 1\cdot84 \times 10^{-18}$, this expression leads to our experimental value of g in molar solution if we assume the plausible values $a = 3 \times 10^{-8}$, $b = 1\cdot5 \times 10^{-8}$ for the dimensions of the water molecule. The observed difference of 3% between the values of g for H_2O and D_2O could be accounted for by a change of about 1% in the factor μ^2/b^3. In the lowest state of the molecules, H_2O and D_2O, the different zero-point energies will give to the former an amplitude of vibration about 2×10^{-10} cm. greater than the latter. This is unlikely to lead to any appreciable difference in dipole moment, but it is reasonable to expect that a difference of the same order of magnitude will occur in the distance of closest approach of two molecules (b in the above equation). The D_2O molecule would thus have an effective radius 1 or 2% greater than the H_2O molecule, which would be sufficient to account for the differences in osmotic behaviour.*

SUMMARY.

(1) The freezing points of solutions of H_2O and D_2O in dioxan have been determined up to a concentration of about $2M$, and compared with the results of similar measurements with the normal solute chlorobenzene.

(2) Both H_2O and D_2O show considerable departures from the laws of ideal solution. The association factor for D_2O is about 3% greater than for H_2O at the same molar concentration.

(2) The values of the osmotic coefficients are consistent with Fuoss's quantitative treatment of dipole interaction. The difference between H_2O and D_2O can be accounted for by the assumption of a small difference in effective radius due to the difference in zero-point energy.

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188. *The Nitrates of Lanthanum, and their Solubilities in Water.*

By J. NEWTON FRIEND.

ALTHOUGH the simple nitrates of the rare-earth elements yield crystalline nitrates readily soluble in water, it is unusual for them to be used for the separation of the elements of the cerium group (Nos. 57 to 62) by fractional crystallisation, the double magnesium or

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* The assumption of different apparent sizes for isotopic molecules is strengthened by the difference of 11% in the molecular volumes of liquid D_2 and liquid H_2 recently reported (Clusius and Bartholomé, *Naturwiss.*, 1934, **22**, 526). Similarly, the molecular volume of solid LiH has been found to be 1·5% greater than that of LiD (Zintl and Harder, *Z. physikal. Chem.*, 1935, **28B**, 478).—The results for water itself are more difficult to interpret owing to the complex structure of both solid and liquid, but the difference in the molecular volumes of the two kinds of ice may be due to the same effect.

Further investigation of the problem (Bell, *Trans. Faraday Soc.*, in the press) shows that the dipole moment of D_2O may be expected to be slightly greater than that of H_2O. This would provide an additional reason for the greater osmotic abnormality of the former.

ammonium nitrates being employed in general. Feit and Praibylla (*Z. anorg. Chem.*, 1905, **43**, 205) recommend the removal of lanthanum from praseodymium by crystallisation from the simple nitrates, the praseodymium salt crystallising in the head fractions. There appear to be only two published data for the solubilities of the salts in water, viz., that at 25°, 100 g. of solution contain 60·18 g. of La(NO$_3$)$_3$ (James and Whittemore, *J. Amer. Chem. Soc.*, 1912, **34**, 1168), and 60·46 g. of Nd(NO$_3$)$_3$ (James and Robinson, *ibid.*, 1913, **35**, 754). Preliminary experiments by the present author did not confirm these figures, and attempts to separate the cerium earths by fractional crystallisation of the simple nitrates have not yielded satisfactory results.

It seemed of interest, therefore, to ascertain the reason for this; it was soon found that the problem is complicated by the existence of two forms of the hexahydrated salt.

Lanthanum nitrate was prepared by dissolution of the oxide in diluted nitric acid. The filtered solution, after concentration on the water-bath, may remain supersaturated for many days. To induce crystallisation, it was seeded with Bi(NO$_3$)$_3$,5H$_2$O, and immediately yielded a crop of the β-hexahydrate, La(NO$_3$)$_3$,6H$_2$O. This somewhat anomalous result may be explained as follows. Although La(NO$_3$)$_3$,5H$_2$O is too unstable to exist alone other than momentarily, it can exist in dilute solid solution in crystals of the corresponding stable bismuth salt (Bodman, *Z. anorg. Chem.*, 1901, **27**, 254). Similarly Bi(NO$_3$)$_3$,6H$_2$O can only exist in solid solution in the corresponding lanthanum salt. On inoculation with Bi(NO$_3$)$_3$,5H$_2$O it is presumed that crystals of the isomorphous La(NO$_3$)$_3$,5H$_2$O are first formed; these immediately change into those of the more stable β-hexahydrate, which now form nuclei for the separation of the remainder
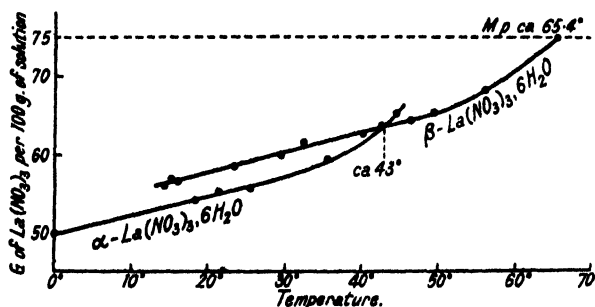
of the salt. That the change is extremely rapid was shown by immediate separation of the crystals and analysis, by determination of their lanthana content by precipitation as oxalate, and subsequent ignition in the usual way. The results always corresponded to the hexahydrate.

Upon prolonged standing at room temperature, the β-salt is transformed into α-La(NO$_3$)$_3$,6H$_2$O, which is stable at the lower temperature and has the lower solubility (see fig.). This salt is also formed from the supersaturated solution by appropriate seeding.

The apparatus used in determining the solubilities has already been described (Friend, J., 1930, 1633); the solubilities are calculated from the lanthana contents of the solutions, this being deemed most accurate as the pure crystals used in preparing the solutions do not undergo perceptible hydrolysis. The saturated solution from the saturation bottle was diluted to 250 c.c. The lanthana was estimated by precipitation from 50 c.c. with excess oxalic acid solution and ignition to oxide. The precipitated oxalate was less granular than that obtained with neodymium and praseodymium, and it was found advisable to digest it on the water-bath for several hours and keep it over-night; finally, it was filtered off in the cold and washed with hot, dilute oxalic acid solution. As a check, a further 50 c.c. were evaporated to dryness in a platinum dish and ignited to oxide. The two methods gave closely similar results, as the following data show :

La$_2$O$_3$ (from oxalate), %	0·5317	0·4230	0·5497	0·9467	0·7564
La$_2$O$_3$ (direct ignition), %	0·5333	0·4236	0·5491	0·9504	0·7587

The latter method invariably yielded a slightly larger amount of lanthana, possibly on account of slight solubility of the oxalate, but more probably because of traces of soluble impurity which the second process would fail to remove. The differences are too small, however, perceptibly to influence the calculated solubilities, *S*, given below. These are expressed as g. of anhydrous salt per 100 g. of solution, and are shown in the fig.

Solid phase, α-La(NO₃)₃,6H₂O.

Temp.	0°	18·4°	21·2°	25·4°	36·4°	42·4°	44·2°
S	50·03	54·18	55·63	55·90	59·12	63·84	65·13

Solid phase, β-La(NO₃)₃,6H₂O.

Temp.	14·4°	15·2°	15·8°	16·0°	23·2°	29·6°	32·2°	40·0°	46·4°	49·4°	56·0°	65·4° *
S	56·27	56·94	56·85	56·74	58·70	60·08	61·34	62·71	64·55	65·17	68·30	75·04

* Melting point.

The transition temperature, α ⟶ β, as read from the solubility curves is approx. 43°.

THE TECHNICAL COLLEGE, BIRMINGHAM.   [*Received, May 17th, 1935.*]

189. *The Specificity of Iron as a Catalyst for the Reaction between Hydrogen Peroxide and Pyrogallol.*

By ALBERT WASSERMANN.

IN the experiments now reported, the reaction between hydrogen peroxide and pyrogallol as catalysed by ferric chloride is studied under various conditions. [Other iron salts have been used as catalyst by Wolf (*Compt. rend.*, 1908, **146**, 784, 1217), Willstätter and Stoll (*Annalen*, 1921, **416**, 64), and Wieland and Franke (*ibid.*, 1927, **457**, 56).]

The main product of the reaction is a brownish dye (or mixture of dyes) soluble in water but only slightly so in ether. Purpurogallin is, at the most, produced in small proportion. If the molar extinction coefficient of the water-soluble dye is taken as of the same order of magnitude as that of purpurogallin, one can calculate (see p. 828) that about 2—5 atoms of oxygen would be required for the formation of 1 mol. of dye. According to Willstätter and Heiss (*Annalen*, 1923, **433**, 27), 3 atoms of oxygen are needed to form 1 mol. of purpurogallin.

During the first stage of the reaction (about 10 mins.) there is an approximate proportionality between the extinction coefficients observed and the iron concentration (see Table II A). It is therefore justifiable to take the extinction coefficients as a measure of the hydrogen peroxide used (cf. papers quoted by Oppenheimer, " Die Fermente und ihre Wirkungen," 5 Aufl., Bd. II, p. 1753). After longer intervals, there is no proportionality; this is connected with the fact that for a given concentration ratio pyrogallol : iron (9 × 10⁻² : 9 × 10⁻⁵ in Table II A) the colour reaches its maximum after 8—10 mins., and then remains constant for at least 2 hours, even although the greater part of the pyrogallol and the hydrogen peroxide is still unchanged ; there is therefore an inhibition of the catalytic activity by the reaction product. The important point is that under the conditions specified no further oxidation of the dye to a colourless substance occurs. But this holds only if the concentration ratio pyrogallol : iron is large, otherwise a fading of the colour is observed. It is probable that the iron is converted by excess of pyrogallol into a relatively inactive complex, incapable of oxidising the dye. This assumption is also in agreement with the fact that the rate of dye formation decreases as the pyrogallol concentration is increased.

It has been observed by Bach (*Ber.*, 1905, **38**, 1878) that the enzyme catalase is inhibited in its activity by pyrogallol. As catalase is an iron compound (Zeile and Hellström, *Z. physiol. Chem.*, 1930, **192**, 171), the inhibition might here too be connected with the formation of an iron–pyrogallol complex.

The dependence of the dye formation on the concentrations of hydrogen-ion and of hydrogen peroxide and on the temperature was also investigated. It is not possible to compare the amount of hydrogen peroxide used under the different conditions, but Tables III—V indicate the minimum hydrogen peroxide consumption.

From the colorimetric measurements, it follows that an extinction coefficient of 5 cm.⁻¹ is produced after 10 mins. at 20° in a solution which is 9 × 10⁻² and 9 × 10⁻⁵*M* with regard to pyrogallol and ferric chloride, respectively, and 0·3*N* in hydrogen peroxide

(p_H 4·1; acetate buffer). For these conditions a hydrogen peroxide consumption of 0·015± 0·005 mols. per litre of solution can be calculated by estimating the hydrogen peroxide remaining after completion of the reaction (*Annalen*, 1933, **503**, 265, Table 16). One mol. of iron, therefore, causes about 0·3 mol. of hydrogen peroxide to react with pyrogallol per second, but under the same conditions it decomposes only 10^{-4} mol. of peroxide per second (*ibid.*, p. 261).

The enzyme peroxydase, which, according to Haldane (*Nature*, 1931, **128**, 175) and Kuhn, Hand, and Florkin (*Z. physiol. Chem.*, 1931, **201**, 255), contains iron in the form of a complex, has no measurable effect on the decomposition of hydrogen peroxide, although it is a very efficient catalyst of the pyrogallol–hydrogen peroxide reaction. Haber and Willstätter's theory of enzyme catalysis (*Ber.*, 1931, **64**, 2854) suggests that other iron compounds as well might be specific. The present experiments show that this is the case, a simple iron salt being about 3000 times more effective a catalyst for the hydrogen peroxide–pyrogallol reaction than for the decomposition of hydrogen peroxide.

EXPERIMENTAL.

The water used as solvent and for rinsing the vessels was twice distilled (quartz condenser). Pyrogallol was purified by sublimation, and hydrochloric and acetic acids by two distillations. The other reagents were the purest supplied by Messrs. B.D.H. The measurements of the extinction coefficients, α, were carried out in the Pulfrich Stuphenphotometer (Zeiss), filter LIII being used. The all-glass uncemented cells (Schott and Gen.) provided with ground stoppers were placed in the air-bath described elsewhere (*Nature*, 1934, **134**, 101). The temperature was constant within ±0·1°.

Relative solubility of the dye formed. 35 Cm. of a 0·09M-pyrogallol, 9 × 10^{-5} M-ferric chloride, and 0·3N-hydrogen peroxide solution (p_H = 4·1; acetate buffer) were kept at 23° for 2 hours : α = 0·90 cm.$^{-1}$. The solution was then extracted three times with 50 c.c. of ether : α of aqueous solution = 0·7 cm.$^{-1}$. The ethereal extracts were concentrated until the volume was 20 c.c. : α = 0·1 cm.$^{-1}$.

For the following experiments, solid pyrogallol, the buffer, or the hydrochloric acid and hydrogen peroxide were mixed and brought to the required temperature. At zero time, the ferric chloride solution was added, and the extinction coefficients continuously observed. Addition of ferric chloride before that of hydrogen peroxide does not affect the results.

The following tables show the effect of varying conditions on the extinction coefficients, which are given in cm.$^{-1}$ at the times stated.

TABLE I.

Purity of Water and Previous Treatment of Ferric Chloride.

H_2O_2 = 0·26N; $C_6H_3(OH)_3$ = 0·090M; p_H = 4·1 (NaOAc = 0·10M; HOAc = 0·30M); $FeCl_3$ = 9·0 × $10^{-6}M$. Temp. = 11·0°. Water : (a) ordinary distilled, (b) once, (c) twice, (d) thrice redistilled. Ferric chloride : stock solution 0·01M, prepared from anhydrous salt and stored at 20° in the dark, (a) for 1 hr., (b) for 8 hrs., (c) for 24 hrs., (d) last solution heated for 2 hrs. at 55°; after this treatment the catalytic efficiency remains constant and this solution was used in all subsequent experiments.

	Time (mins.)	(a).	(b).	(c).	(d).
Water	10	0·120	0·100	0·086	0·092
Ferric chloride	10	0·233	0·218	0·170	0·072

TABLE II.

Variations in Concentration (A) of Ferric Chloride, (B) of Pyrogallol.

(A) Conditions as in Table I. (B) $FeCl_3$ = 9·0 × $10^{-6}M$; other conditions as in Table I.

Time (mins.).	(A) $FeCl_3$, mols./l.			(B) $C_6H_3(OH)_3$, mols./l		
	9·0 × 10^{-4}	9·0 × 10^{-6}	9·0 × 10^{-6}	0·90	0·090	0·0090
2	3·0	0·38	0·030	0·19	0·38	0·62
4	5·5	0·62	0·042	0·21	0·62	0·79
6	8·2	0·74	0·052	0·23	0·74	0·88
8	10·2	0·81	0·064	0·27	0·81	0·94
10	12·3	0·84	0·072	0·30	0·84	1·00
15	17·0	0·86	0·096	0·37	0·86	1·09
20	—	0·88	0·120	0·42	0·88	1·12
30	—	0·90	0·166	0·58	0·90	1·18

In a 0·0087*M*-pyrogallol and 9 × 10⁻⁴*M*-ferric solution (other conditions as in Table I) after some time a fading of the colour first formed is observed. If, however, the pyrogallol concentration is increased to 0·09*M*, and the iron concentration decreased to 9 × 10⁻⁵*M*, then the colour intensity observed after about 10 mins. remains constant. Under the conditions specified, α (10 mins.) = 0·84 cm.⁻¹ and α (240 mins.) = 0·90 cm.⁻¹. If, after 240 mins., the solution is made 2 × 10⁻⁴*M* with respect to ferric chloride by further addition, then a fresh increase of the extinction coefficient is observed.

TABLE III.

Effect of Hydrogen-ion Concentration.

p_H 4·6—p_H 3·6, acetate buffer (0·1*M* in reaction mixture); p_H 2—p_H 0, hydrogen chloride; other conditions as for Table I.

Time (mins.).	4·6.	4·1.	p_H. 3·6.	2·0.	0·0.	Time (mins.).	4·6.	4·1.	p_H. 3·6.	2·0.	0·0.
4	0·021	0·042	0·060	0·42	0·050	20	0·045	0·120	0·154	1·60	0·38
10	0·033	0·072	0·100	0·93	0·16	30	0·050	0·166	0·198	1·91	0·60
15	0·040	0·096	0·130	1·30	0·26						

TABLE IV.

Hydrogen Peroxide Concentration.

$FeCl_3 = 9·0 × 10^{-5}M$; other conditions as for Table I.

Time (mins.).	H_2O_2, N. 2·6.	0·26.	0·026.
10	1·33	0·81	0·77

TABLE V.

Temperature.

Conditions as for Table I.

Time (mins.).	11·0°.	25·0°.
10	0·072	0·190

The value of 5 cm.⁻¹ for the extinction coefficient of the solution specified on p. 826 was estimated by using the results of Tables I, II, and V. It has been found (*Annalen*, 1933, 503, 265) that for 17·5 c.c. of 0·26N-hydrogen peroxide, 0·0087*M*-pyrogallol, and 9 × 10⁻⁵*M*-ferric chloride solution (p_H 4·1; 20°) an extinction coefficient of 1·12 cm.⁻¹ corresponds to a consumption of 6 × 10⁻⁵ mols. of hydrogen peroxide. From this result, the hydrogen peroxide consumption given on p. 827 has been calculated.

It has been found that the molar extinction coefficient of purpurogallin in ether is 800 l./g.-mol./cm. for 470 mμ. This value and the hydrogen peroxide consumption as calculated above were used for the estimation of the number of oxygen atoms which are required for the formation of 1 mol. of the unknown dye (see p. 826).

I wish to thank Professor C. K. Ingold, F.R.S., and the Imperial Chemical Industries, Ltd., for their help. Messrs. Zeiss (Jena) kindly lent the Stuphenphotometer.

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190. *The Mechanism of Additions to Double Bonds. Part I.*
*Thermochemistry and Kinetics of a Diene Synthesis.*

By ALBERT WASSERMANN.

THE important example of 1 : 4-addition to a conjugated system (*a*), known as a diene synthesis, where the addendum is a compound containing a reactive double bond (*b*), was
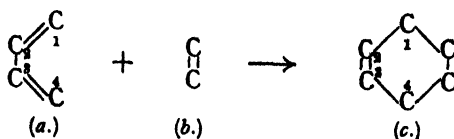
investigated chiefly by Diels and Alder. The present communication attempts to provide an explanation why addition should not occur also in the 1 : 2-position, the typical case

investigated being the reaction between *cyclo*pentadiene (I) and benzoquinone (II) to yield *cyclo*pentadienebenzoquinone (III).*

(I.)   (II.)   (III.)
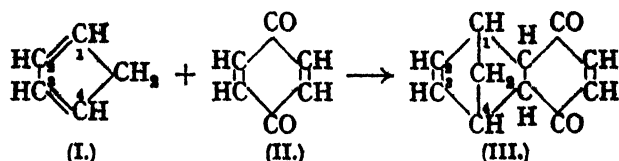
Section 1 deals with the determination of the heat of the 1 : 4-addition of benzoquinone to *cyclo*pentadiene, and also with that of the hypothetical 1 : 2-addition. Both reactions are exothermic, and there is therefore no thermodynamic reason for the preferential 1 : 4-addition. In Section 2, the kinetics of the reaction are investigated, and it is shown that a second-order association, relatively insensitive to catalysts, light, or magnetic field, is involved. The activation energy in alcohol or benzene is 13—14 kg.-cals. Section 3 gives the calculation of the dipole induction energy for different mutual orientations of the *cyclo*pentadiene and the benzoquinone molecule. For orientations which might lead to the 1 : 4-addition product, the induction energy is greater than for those suitable for 1 : 2-addition. Hence, the conclusion is drawn that the activation energy of the 1 : 2-addition is greater than that of the 1 : 4-addition, and that this is the explanation for the observed course of the reaction.

The method employed here will, of course, not be applicable to the general case of addition of double bonds to conjugated systems if all the dipole moments of the bonds of the reacting molecules are immeasurably small (*e.g.*, dimerisation of *cyclo*pentadiene). If, however, the reacting molecules contain, like benzoquinone, polar groups (*e.g.*, maleic anhydride), then a calculation of the induction energies will in many cases be useful.

1. *Thermochemistry of the* cyclo*Pentadiene–Benzoquinone Reaction.*

In order to determine the heat of the additive reaction, the heats of formation of the three molecules from carbon (^5S),† hydrogen, and oxygen must be known. For the calculation of the heats of formation from the heats of combustion (corrected for the gaseous state) the heat of the reaction $C(^5S) + O_2 = CO_2$ was taken as 270 kg.-cals. (cf. Kohn and Guckel, *Z. Physik*, 1924, **27**, 306; Heitler and Herzberg, *ibid.*, 1929, **53**, 52; Pauling, *J. Amer. Chem. Soc.*, 1932, **54**, 3570; Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606).

The bond energies given by Pauling and Sherman (*loc. cit.*) were used for the additive calculation of the heats of formation. For the C=O bond in quinone and in (III), however, another value, *viz.*, 183 kg.-cals. was taken. This figure is an average of the C=O value given by Pauling and Sherman and of that of six cyclic ketones (suberone, β-methyl-*cyclo*hexanone, β-methyl*cyclo*pentanone, *cyclo*pentanone, and *cis*- and *trans*-β-decalone).

The heat of combustion of gaseous *cyclo*pentadiene was found to be 707 ± 7 kg.-cals./ mol. (see p. 839), whence the heat of formation is 1153 ± 7 kg.-cals., whereas addition according to $2(C=C) + 3(C-C) + 6(C-H)$ leads to 1152 kg.-cals. The resonance energy of a system of two conjugated double bonds is 8 kg.-cals. according to Pauling and Sherman (*loc. cit.*, p. 682). This value is probably too high, for the heats of formation of butadiene and isoprene calculated from the heats of combustion (Landolt–Börnstein–Roth, " Tabellen," II, Suppl.) are, if anything, a little lower than those obtained by adding the bond-energies. The close agreement between the calculated and the found heat of formation of *cyclo*pentadiene is probably fortuitous.

In correcting the heat of combustion of solid benzoquinone (" Tabellen," I, Suppl.) for the gaseous state, the heat of sublimation given by Coolidge and Coolidge (*J. Amer.*

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* For formation and constitution of this compound, see Albrecht, *Annalen*, 1906, **348**, 1; Diels, Blom, and Koll, *ibid.*, 1925, **443**, 247; Diels and Alder, *ibid.*, 1928, **460**, 98; Diels, Alder, and Stein, *Ber.*, 1929, **62**, 2337; Alder and Stein, *Annalen*, 1931, **485**, 218; 1933, **501**, 253.

† The exact description of the electronic state of quadrivalent carbon is $2s2p^3$ ^5S.

Chem. Soc., 1927, **49**, 103) was used., The experimental heat of formation is 1405 kg.-cals., and the value calculated from $2(C{=}O) + 2(C{=}C) + 4(C{-}C) + 4(C{-}H)$ is 1403 kg.-cals.

The heat of combustion of (III) was found to be 1336 ± 1 kg.-cals./mol. (see p. 839). The heat of sublimation of quinone is 15 kg.-cals., and the heat of vaporisation of *cyclo*pentadiene 7 kg.-cals. (Trouton). It can be assumed that the heat of sublimation of (III) is 22 ± 5 kg.-cals., for Dunkel (*Z. physikal. Chem.*, 1928, **138**, 44) has pointed out that the molecular forces of certain types of organic compound are additive, and this can be explained by a theoretical treatment of cohesion forces given by London (*Z. Physik*, 1930, **63**, 245; *Z. physikal. Chem.*, 1930, *B*, **11**, 222). The heat of combustion of the gaseous addition compound is therefore 1358 ± 6 kg.-cals., and this gives a heat of formation of 2579 ± 6 kg.-cals., whereas addition according to $2(C{=}C) + 11(C{-}C) + 10(C{-}H) + 2(C{=}O)$ leads to 2589 kg.-cals. The difference of 10 ± 6 kg.-cals., if real,[*] is doubtless connected with the ring-strain in *bicyclo*heptene systems. Alder and Stein (*Ber.*, 1934, **67**, 613) deduce for similar compounds a ring-strain of 6—7 kg.-cals.

The compound (III) contains a system of three conjugated double bonds $O{=}C{-}C{=}C{-}C{=}O$. A comparison of the experimental and the calculated heat of formation of methyl fumarate shows that such a system has no thermochemically measurable resonance-energy : $2(C{-}C) + (C{=}C) + 8(C{-}H) + 2(C{=}O)$ [†] $+ 4(C{-}O) + 2$(resonance energy CO_2Me) [‡] $= 1859$ kg.-cals.; experimental heat of formation (cf. Wassermann, *Z. physikal. Chem.*, 1930, **140**, 419) $= 1857$ kg.-cals. Table I summarises the numerical details.

TABLE I.

Experimental and calculated heats of formation of cyclopentadiene *(I)*, benzoquinone *(II)*, *and* cyclopentadienebenzoquinone *(III)*.

	Heat of combustion, corr. for gaseous state (kg.-cals./mol).	Heat of formation from C(^1S), H, and O, kg.-cals.		Remarks.
		From heat of combustion.	From bond-energies.	
(I)	707 ± 7	1153 ± 7	1152	No resonance-energy.‡
(II)	672 ± 1	1405 ± 1	1403	No resonance-energy.
(III)	1358 ± 6	2579 ± 6	2589	No resonance-energy; ring-strain.

‡ Comparison of found and calculated heats of formation of isoprene and butadiene.

From Table I it can be seen that the calculated and the found heats of formation agree within the possible experimental error if allowance is made for the ring-strain in (III). By using this result, the heat of the reaction *cyclo*pentadiene (gas) + benzoquinone (gas) = *cyclo*pentadienebenzoquinone (gas) can be estimated as follows : Energy gain $= 2(C{-}C)$; energy consumption $= 2[(C{=}C) - (C{-}C)] +$ ring-strain in *cyclo*pentadienebenzoquinone; heat of reaction = difference = 24 kg.-cals. As the heats of formation of certain gaseous endo- and exo-isomeric compounds are nearly identical (Alder and Stein, *Ber.*, 1934, **67**, 613), it is very probable that this heat of reaction is independent of the steric configuration of the product.

A similar calculation for the heat of the hypothetical 1 : 2-addition product requires the thermal equivalent of the ring-strain in the *cyclo*butane ring. There are four liquid *cyclo*butane derivatives whose heats of combustion are known, *viz.*, *cyclo*butylcarbinol, acetyl*cyclo*butane, *cyclo*butanecarboxylic acid, and methyl *cyclo*butane-αβ-dicarboxylate (cf. Landolt–Börnstein–Roth, " Tabellen "; Beilstein, Vol. V, Erg.-bd., p. 5, note 1). For the additive calculation of the heats of formation, the bond strengths and the resonance energy for the carboxyl and the carbomethoxy-group given by Pauling and Sherman (*loc. cit.*) were used. Comparison with the experimental heats of formation gives about 15 kg.-cals. (average) for the ring-strain in the *cyclo*butane ring. By taking this value and calculating as before, the following result is obtained : *cyclo*pentadiene (gas) + benzoquinone (gas) = hypothetical 1 : 2-addition product (gas) + 19 kg.-cals.

[*] The conclusion reached above is independent of the possibility of the thermochemical determination of the ring-strain in (III).

[†] 178 Kg.-cals.   [‡] Cf. Pauling and Sherman, *loc. cit.*

The absolute values of the calculated heats of reaction are, of course, only a very rough approximation. The energy difference between C^3P and C^5S, which was employed in the calculation, is not accurately known. Heitler and Herzberg's value (*loc. cit.*) which was used seems to be much too small (cf. van Vleck, *J. Chem. Physics*, 1934, **2**, 20, 297). Further, a possible change of the zero-point energy of the system before and after the addition process should be considered for a more accurate calculation. The comparison of the values for the heat of 1 : 4- and 1 : 2-addition, however, is not much affected by these uncertainties, and the calculation shows, therefore, that both the 1 : 4- and the 1 : 2-addition of benzoquinone to *cyclo*pentadiene are exothermic. This might have been expected from a study of the models, as the ring-strain in the *cyclo*butane ring is nearly the same as in camphor (cf. Freudenberg, " Stereochemie," 1933, p. 790), which contains an *endo*methylene bridge similar to that in (III).

The assumption that the equilibrium between *cyclo*pentadiene, benzoquinone, and their hypothetical 1 : 2-addition product lies far on the side of dissociation is therefore so improbable that it cannot be used to explain the actual course of the reaction.

2. *Kinetics of the* cyclo*Pentadiene–Benzoquinone Reaction.*

The following reactions have to be considered in a mixture of quinone and *cyclo*pentadiene in the presence of air :

(i) (I) + (II) $\longrightarrow$ (III) ; (ii) (III) $\longrightarrow$ (I) + (II) ; (iii) (III) + (I) $\longrightarrow$ di*cyclo*pentadienebenzoquinone (Albrecht, *loc. cit.*) ; (iv) 2(I) $\longrightarrow$ di*cyclo*pentadiene (cf. Alder and Stein, *Annalen*, 1933, **504**, 316) ; (v) (I) + O$_2$ $\longrightarrow$ *cyclo*pentadiene oxide (Engler and Frankenstein, *Ber.*, 1901, **34**, 2938).

In a preliminary communication (*Ber.*, 1933, **66**, 1392), it was shown that the velocity coefficient of reaction (i) at 20° is, according to the solvent, 0·002—0·2 l./g.-mol./sec., and that the rate of (iii) in benzene solution is about 100 times smaller. Further, a series of measurements (Stobbe and Reuss, *Annalen*, 1901, **391**, 151 ; Barret and Burrage, *J. Physical Chem.*, 1933, **37**, 1029 ; Schulze, *J. Amer. Chem. Soc.*, 1934, **56**, 1552) shows that the rate of (iv) is about 10^4 times smaller than that of (i). Reaction (v) is still slower than (iv) (cf. Stobbe and Dünnhaupt, *Ber.*, 1919, **52**, 1436). In order to obtain information as to the relative rate of reaction (ii), the amount of benzoquinone used during the attainment of a steady state in an equimolar mixture of it with *cyclo*pentadiene was measured. At 20°, 40°, and 50°, 96—99% of the benzoquinone used was found to have reacted. *cyclo*-Pentadienebenzoquinone is known to isomerise easily. This is connected with the mobility of the γ-hydrogen atoms (Diels, Alder, and Stein, *loc. cit.*), and also possibly with the wandering of double bonds without migration of hydrogen atoms and with steric changes. On this account, in addition to the foregoing determination, the *cyclo*pentadienebenzo-quinone formed (under the conditions of the kinetic measurements) was also isolated ; the yield was 92—94% of the theoretical.

As benzoquinone is much more highly coloured than the product (III), the course of the additive reaction can be followed colorimetrically (cf. Wassermann, *Nature*, 1934, **134**, 101), and it was found to be of the second order (time for half-change inversely proportional to equimolar initial concentration). The velocity coefficients (k) given in Table II are accurate to within 5—7%, and the critical increments as quoted below to about ± 1 kg.-cal.

TABLE II.

Velocity coefficients and half-change periods (at 20·4°).

Solvent.	Initial concn., g.-mol /l. (II).	(I)	k, 1 /g. mol / sec.	Half-change, sec. $\times 10^{-2}$.	Solvent.	Initial concn , g -mol /l (II).	(I)	k, 1 /g mol / sec	Half-change, sec $\times 10^{-2}$.
C_6H_6	0·0500	0·0500	0·0072	28	EtOH	0·0100	0·0100	0·030	34
	0·0200	0·0200	0·0067	75		0·0100	0·00330	0·028	27
	0·0200	0·0100	0·0065	62		0·00500	0·00500	0·030	67
	0·0100	0·0100	0·0067	150		0·00200	0·00200	0·030	168
	0·00200	0·00200	0·0065	768					

The proportionality of log k to $1/T$ is shown in Fig. 1. The constants of the Arrhenius equation, $k = Ze^{-E/RT}$ are :

Solvent.	Z (l./g.-mol./sec.).	E (kg.-cals.).	Solvent.	Z (l./g.-mol./sec.).	E (kg.-cals.).
C_6H_6	$2\cdot7 \times 10^8$	$14\cdot2$	EtOH	$8\cdot8 \times 10^7$	$12\cdot7$

The rate of reaction was not affected by the materials of the walls of the absorption cells, by the purity of the solvents or of the reactants, by light, or by a strong magnetic field. The rate at which the yellow colour in the equimolar mixture of benzoquinone and *cyclo*pentadiene faded was unaffected by the addition of iodine (in the dark or in the light), $\alpha\alpha'$-dipyridyl, p-toluenesulphonic acid, ferric chloride, manganous chloride, cupric chloride, *trans*-stilbene, iodoacetic acid, or bromoacetic acid. Chloroacetic acid, phenol, and hydrochloric acid produced a slight increase of the rate, and pyridine a slight decrease.

It is well known that some additions to double bonds and some polymerisations of ethylene derivatives are chain reactions. However, such reactions are often characterised by bad reproducibility of the kinetic measurements, *i.e.*, by great sensitivity to external influences or to traces of foreign substances. The experimental results therefore make it improbable that the present reaction is a chain reaction. In particular, peroxidic intermediate compounds seem to play no part in the kinetics; for if they did, it might be expected, by analogy with other reactions, that iron, copper, or manganese salts, possibly also $\alpha\alpha'$-dipyridyl or pyridine, would be efficient catalysts, and even small amounts of phenol or stilbene would inhibit the reaction.

FIG. 1.

Temperature dependence of the velocity coefficients.

3. 1 : 4- *and* 1 : 2-*Addition of Benzoquinone to* cyclo*Pentadiene.*

The kinetic measurements recorded in the preceding section show that the velocity coefficient of the reaction is determined by the two constants Z and E of the Arrhenius equation, which for a given solvent are dependent only on characteristic properties of the reacting molecules. This experimental result justifies the assumption that the velocity coefficient of the hypothetical 1 : 2-addition of benzoquinone to *cyclo*pentadiene is also characterised by only two constants. We therefore have :

$$\left.\begin{array}{llllllll} \text{1 : 4-addition} & . & . & . & . & . & . & k_{1:4} = Z_{1:4}\,e^{-E_{1:4}/RT} \\ \text{1 : 2-addition} & . & . & . & . & . & . & k_{1:2} = Z_{1:2}\,e^{-E_{1:2}/RT} \end{array}\right\} \quad (1)$$

It is necessary for the following considerations to determine the mutual orientations of the benzoquinone and the *cyclo*pentadiene molecules most suitable for the regrouping of the electrons corresponding to the addition. If the $C\!\!=\!\!C$ bond of the quinone is near the atoms I and IV of the *cyclo*pentadiene, then 1 : 4-addition will result, whereas 1 : 2-addition requires that the $C\!\!=\!\!C$ bond should be close to the atoms I and II. The juxta-position of reacting centres is not, however, the sole determining factor. The most suitable orientations will be those in which mutual interpenetration of the outsides of all the other atoms of the reactants occurs to a minimum extent. Figs. 2—4 show such orientations drawn to scale in plan and side-elevation. The lengths of the individual bonds have been taken to be the same as those determined for isolated molecules.

1 : 4-*Addition.*—If the distance BIV in Fig. 2 is 2·0 Å., then the distance GX or HX is 1·72 Å. and BX or CX 1·90 Å. The orientation of Fig. 3 is also possible; the distance BIV being assumed to be, as in Fig. 2, 2·0 Å., then the distance EX or FX would be 1·6 Å. The steric course of the reaction depends on whether the orientation of the reacting molecules at the moment of impact is that of Fig. 2 or of Fig. 3. This, of course, only holds

when the possibility of a subsequent rearrangement of the incompletely stabilised product is excluded. The interesting subject of *endo-exo*-isomerism of the addition compound is, however, not regarded as within the scope of this paper.

Rotation of the *cyclo*pentadiene about an axis passing through I–IV (Fig. 2) would soon meet with considerable resistance, as repulsive forces between atoms increase rapidly with decreasing distance. For instance, if the diene is rotated through 20° into the plane α', then the distance HX or GX becomes 1·3 Å. Again, an equal rotation into the plane α'' decreases the distances $EVII$ and $FVIII$ to 1·4 Å. and DII and $AIII$ to 1·7 Å. Considerations of this nature apply to other BIV distances and to the orientation of Fig. 3. Therefore, mutual orientations of *cyclo*pentadiene and benzoquinone suitable for 1 : 4-addition are improbable when the angle between the planes α' or α'' and β is greater than
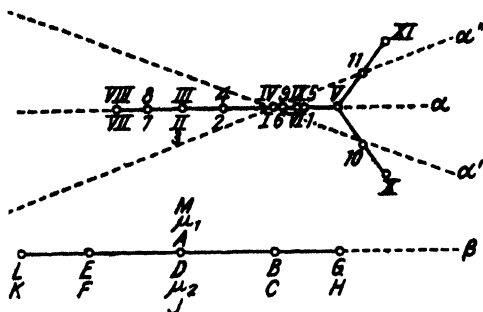
FIG. 2.　　　　　　FIG. 3.
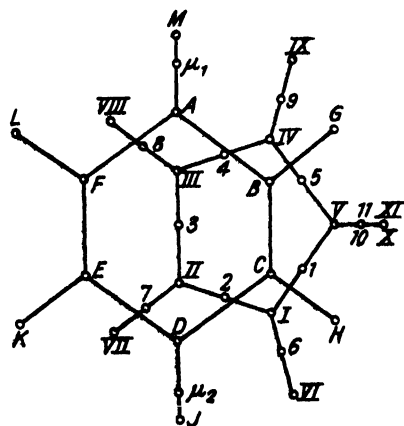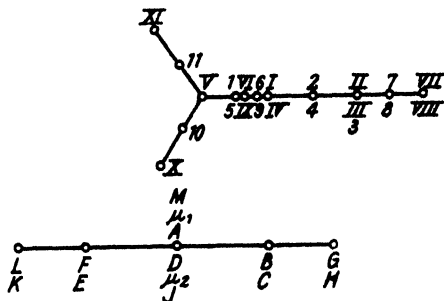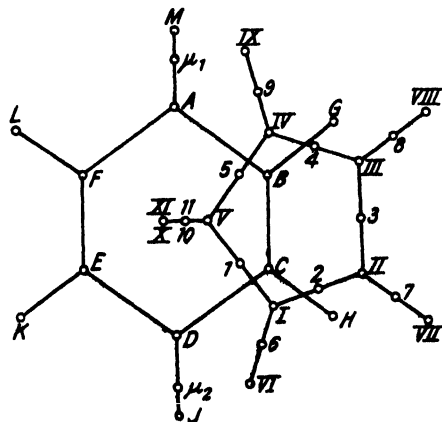
An orientation suitable for 1 : 4 *addition.*　　　*Alternative orientation suitable for* 1 : 4 *addition.*

about 20°, and the most favourable orientations will be those in which the planes of the rings are nearly parallel.

1 : 2-*Addition*.—In the orientation of Fig. 4, the angle between the planes α and β is 20°, and the distance BI or CII 2·0 Å. The distance GVI or $HVII$ is 1·75 Å., and AX is 1·55 Å. Any material decrease in the angle between α and β is not possible, for the repulsive forces between A and X would certainly increase rapidly as soon as AX becomes smaller than about 1·4 Å. An increase in the angle would, however, be less strongly resisted than in the orientation of Fig. 2. Rotation of the *cyclo*pentadiene through 160° (in the direction of the arrow a) about an axis passing through I–II leads to another orientation suitable for 1 : 2-addition.

Different values of Z (equation 1) for two such similar reactions as the 1 : 4- and the 1 : 2-addition could, when both reactions occur in the same solvent, be ascribed only to steric differences. The above discussions of the possible mutual orientations show, there-

fore, that $Z_{1:2}$ cannot be much smaller than $Z_{1:4}$, and that a difference in the Z values cannot therefore be used to explain the predominance of 1 : 4-addition actually found.

In attempting to base an explanation on a difference between the activation energies $E_{1:2}$ and $E_{1:4}$, it is assumed that benzoquinone and *cyclo*pentadiene first take up an intermediate configuration (transition complex) which can then either decompose into the components, or else give rise to the reaction products by a spontaneous regrouping of the electrons. The smallest energy increment necessary to produce the intermediate configuration can be taken as the activation energy of the reaction.

The electrons of the double bond BC are doubtless rendered so mobile by the proximity of the two carbonyl groups that a regrouping of electrons can occur at relatively large separations of the molecules.* This effect will be the same whether the benzoquinone is added in the 1 : 4- or in the 1 : 2-position of the *cyclo*pentadiene. The next step, therefore, is to consider the influence of the carbonyl group, not on the bonds of the quinone, but on the various bonds of the *cyclo*pentadiene. The two dipoles of the carbonyl groups will induce other dipoles, and this will effect a certain attraction between the benzoquinone and the *cyclo*pentadiene molecules.

In order to calculate the energy corresponding to this dipole induction in the positions of Fig. 2 and Fig. 4, the following assumptions were made : the dipole moment of the carbonyl group in benzoquinone is $2 \cdot 8 \times 10^{-18}$ e.s.u. and is localised symmetrically between the imaginary circumferences (cf. Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1910) of the carbon and the oxygen atoms at the points μ_1 and μ_2; there is no measurable permanent dipole moment corresponding to the C–H bonds of the cyclic molecules

FIG. 4.
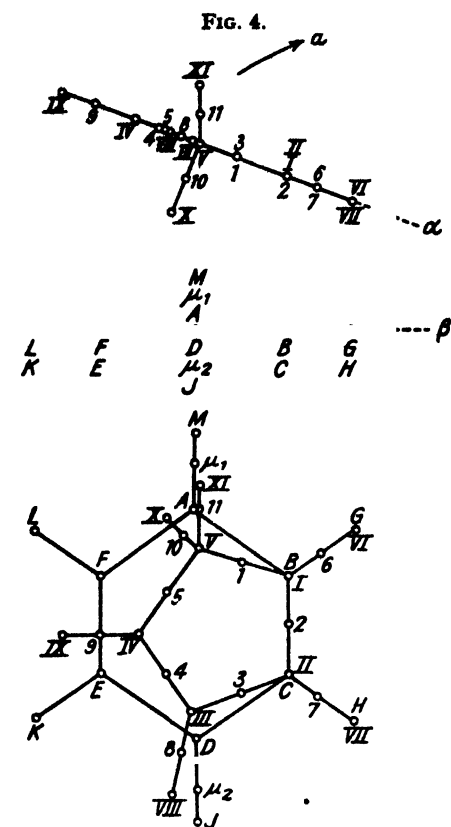
An orientation suitable for 1 · 2 addition.

involved ; the bonds of the *cyclo*pentadiene are treated as polarisable spheres located in the middle of each bond at the points 1–11; the polarisability is isotropic; the dipoles induced in the various bonds have no action on one another. J, the induction energy is given by

$$J = PF^2/2 \qquad \cdots \cdots \cdots \quad (2)$$

The polarisability P is obtained from the octet refractions (Smyth, *Phil. Mag.*, 1925, **50**, 301; Fajans and Knorr, *Ber.*, 1926, **59**, 249) :

Bond.	C—C.	C=C.	C—H.
$P \times 10^{24}$ (cm.^{3})	0·478	1·64	0·671

In calculating the electric intensity F at the points m ($m = 1$–11 in Fig. 2 and Fig. 4), the x-axis was chosen to pass through μ_1 and μ_2, while the y-axis lay in the μ_1–μ_2–m-plane (cf. Fig. 5). The following equations hold for F_x and F_y (cf. Jeans, " Electricity and Magnetism," Cambridge, 1925; Smallwood and Herzfeld, *loc. cit.*) :

$$F_x = \frac{\mu_1}{r_1^3} (3 \cos^2 \delta_1 - 1) - \frac{\mu_2}{r_2^3} (3 \cos^2 \delta_2 - 1) \left.\begin{array}{c} \\ \\ \\ \end{array}\right\}$$

$$F_y = \frac{3\mu_1}{r_1^3} \sin \delta_1 \cos \delta_1 + \frac{3\mu_2}{r_2^3} \sin \delta_2 \cos \delta_2 \qquad \cdots \cdots \quad (3)$$

* Of course the separation will also depend on the mobility of the electrons of the *cyclo*pentadiene.

The induction energies as calculated by (2) and (3) are given in Table III for different distances d characterising the degree of separation of the molecules. Measures for these distances are *BIV* (= *CI*) in Fig. 2 and *BI* (= *CII*) in Fig. 4.

TABLE III.

Induction energies corresponding to different intermediate configurations in the cyclopentadiene–benzoquinone *reaction.*

1 : 4-Addition, intermediate	{ Distance d (Å.)	2·33	2·00	1·80
configuration, Fig. 2	{ Induction energy (kg.-cals./mol.)	−3·3	−6·7	−9·6
1 : 2-Addition, intermediate	{ Distance d (Å.)	2·33	2·00	1·80
configuration, Fig. 4	{ Induction energy (kg.-cals./mol.)	−2·4	−3·7	−5·1

In order that the reacting molecules may approach one another so closely that addition can take place, considerable repulsive forces have to be overcome by the help of kinetic energy of translation, dispersion forces (cf. London, *loc. cit.*), and induction energy. The figures of Table III show that the induction energy is greater for that orientation which will result in 1 : 4-addition than for that giving 1 : 2-addition. We assume that the dispersion forces in the orientation of Fig. 4 are not greater than in that of Fig. 2.* It then seems reasonable to conclude from the calculated induction energies that the activation energy is greater for the 1 : 2- than for the 1 : 4-addition and that, as a first approximation, the difference in the activation energies equals the difference in the induction energies. If it be further assumed that in equations (1) $Z_{1:2} = Z_{1:4}$, then the following ratios of the velocity constants are obtained from the data in Table III :

FIG. 5.

In equation (3) the distance $r_1 = \mu_1 m$ and $r_2 = \mu_2 m$.

Distance d (Å.)	2·33	2·00	1·80
$k_{1:4} : k_{1:2}$ at 20°	~5	~170	~2200

The differences in the rates calculated from the induction energies are therefore sufficient to explain the predominant formation of the 1 : 4-addition product, provided the distance d be not much greater than 2 Å.
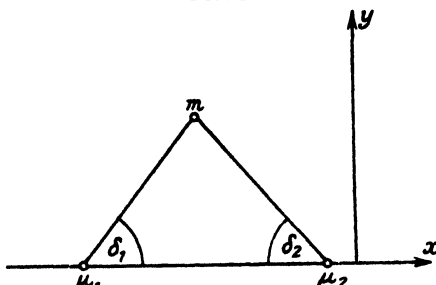
EXPERIMENTAL.

The *cyclo*pentadienebenzoquinone used was purified by recrystallisation from methyl alcohol and light petroleum until the colour was constant. Shaking of the light petroleum (b. p. 60—80°) solution with calcium oxide, magnesium oxide, calcium carbonate, Fasertonerde (Merck), sucrose, or charcoal (Merck) then produced no diminution of colour. The colour measurements throughout were carried out with Zeiss's Pulfrich Stufenphotometer and filter S_{47}. The colour is a much more sensitive criterion of the purity of the substance than the m. p.; *e.g.*, two specimens, both of m. p. 76—77°, gave molar extinction coefficients (ε) of 0·122 and 0·144 l./g.-mol./cm. (benzene). The ε value (l./g.-mol./cm.) of the purest specimen was 0·0578 in benzene and ~0·1 in ethyl alcohol. Beer's law holds in both solvents, and at room temperature the colour of a benzene solution remains constant for many hours. In benzene the value of ε was unaffected by temperature changes between 11° and 50°. In alcohol, the colour deepens rapidly. The extinction coefficient was determined as soon as possible after preparation of the solution.

The heats of combustion in Tables IV and V were determined at 20° (cf. p. 839) by using oxygen at 38 atm. in a bomb with a water equivalent of 2806·2 ± 0·6 cals./degree.

* It will be shown in a later paper that this assumption holds true.

TABLE IV.

Heat of combustion of cyclo*pentadienebenzoquinone.*

Weight, g.	Δt (corr.).	Heat of combustion, cals.		
		Total.	Corr.	Cals./g. (const. vol.).
0·60750	1·6755°	4701·8	34·9	7682·0
0·60480	1·6630	4666·7	23·9	7676·5 } Mean
0·60375	1·6625	4665·3	31·7	7674·5 { 7677·0
0·55760	1·5360	4310·5	30·5	7676·0

The polymeric *cyclo*pentadiene used for the preparation of the monomeride had been prepared by Fraenkel and Landau (Berlin) and Light (London). An all-glass distillation apparatus with an efficient fractionating column was used. The apparatus was first evacuated and then filled with nitrogen. The distillate, too, was kept in nitrogen. After the second distillation, the b. p. was constant to within a few tenths of a degree, and agreed with the accepted value. Since the combustion took place some 2 or 3 days after the distillation, some polymerisation had occurred. It was therefore necessary to estimate this amount (cf. Stobbe and Reuss, *loc. cit.*; Schulze, *loc. cit.*) by determining the refractive index of a control sample which had undergone exactly parallel treatment. As the heat of combustion of di*cyclo*pentadiene is known (Becker and Roth, *Ber.*, 1934, 67, 627; Alder and Stein, *loc. cit.*), that of *cyclo*pentadiene can be calculated if the heat of combustion of a mixture of the two in known proportion is determined. In order to calculate the composition of the mixture from $n_D^{20°}$, it is necessary to get $n_D^{20°}$; for this the data of Stobbe and Reuss (*loc. cit.*), v. Auwers (*Ber.*, 1912, 45, 3078), and Zelinsky and Lewina (*Ber.*, 1933, 66, 477) were used.

TABLE V.

Heat of combustion of cyclo*pentadiene.*

Sample.	$n_D^{22·0°}$.	Di*cyclo*pentadiene in mixture, %.	Heat of combustion, cals./g.	
			Mixture.	*cyclo*Pentadiene.
a	1·4937	72·6	10,475	10,570 } Mean
b	1·4928	71·5	10,528	10,770 } 10,600 ± 100
c	1·4966	76·8	10,441	10,480

After the combustions, carbon monoxide could not be detected, but a little lamp black was found. However, the heat of combustion of this was only about 0·2% of the total heat of combustion. The uncertainty of the values in Table V is connected with the great volatility of the liquid * and relatively high rate of polymerisation. The determination of the composition of the mixture at the moment of combustion is therefore subject to an error of 1%.

Different specimens of benzoquinone (Kahlbaum, Merck, B.D.H.) were crystallised 1—3 times from hexane and carefully dried. Consistent results were obtained with the different materials. Table VI gives the ϵ values : Beer's law held for the given range of concentration, and no temperature effect could be observed (see last col.).

TABLE VI.

Molar extinction coefficients of benzoquinone.

Solvent.	ϵ (l./g.-mol./cm.).	No. of concns. investigated.	Range of concn. (g.-mol./l.).	Max. temp. range.
Benzene	17·0	9	0·1—0·0005	8—50°
Alcohol	13·4	8	0·05—0·002	11—40

For the preparation of the *cyclo*pentadiene solutions the ice-cooled distillate was weighed into a measuring flask as quickly as possible. The flask was again cooled with ice, the stopper removed, and the solvent added. The solutions prepared were as dilute as possible and kept at 0°, and were, generally, not more than a few hours old when measured.

In order to obtain the total amount of benzoquinone converted, the extinction coefficient of a solution of equimolar quantities of *cyclo*pentadiene and benzoquinone in the steady state was measured. We have $\alpha_S = (a - x_S)\epsilon_Q + x_S\epsilon_C$, where x_S is the amount of quinone reacting, α_S the extinction coefficient in the steady state, and a the initial concentration of benzoquinone or *cyclo*pentadiene : ϵ_Q and ϵ_C are the respective molar extinction coefficients of benzoquinone and condensation product.

* The substance had to be introduced into the bomb in sealed glass bulbs.

TABLE VII.

Amount of benzoquinone used during attainment of a steady state in its equimolar mixture with cyclo*pentadiene.*

	Solvent: Benzene.					Solvent: Ethyl alcohol.			
Temp.	Initial concn. (g.-mol./l.).	Time (hrs.).	a_s (cm.$^{-1}$).	Quinone used, %.	Temp.	Initial concn. (g.-mol./l.).	Time (hrs.).	a_s (cm.$^{-1}$).	Quinone used, %.
20°	0·0500	620	0·0230	98	20°	0·100	20	0·063	96
20	0·0503	120	0·0409	96	20	0·100	120	0·065	96
20	0·199	72	0·0435	99	40	0·110	1	0·076	95
20	0·518	72	0·123	99	40	0·110	3·5	0·073	96
20	1·04	100	0·469	98					
50	0·310	7	0·130	97					

For the isolation of the product, the solvent was evaporated at room temperature, and the residue crystallised from petroleum (b. p. 60—80°) or from a little methyl alcohol. The m. p. was then 72—75°, not depressed by admixture with pure *cyclo*pentadienebenzoquinone. Repeated recrystallisations of the specimens gave products of m. p. *ca.* 76—77°.

If the mixtures of the reactants were heated at 40° or 50° for periods longer than those indicated in Table VIII (*e.g.*, 20 hrs.), the crystals obtained differed from Albrecht's *cyclo*pentadienebenzoquinone in having greater solubility in methyl alcohol and markedly lower m. p., *viz.*, 55—65° : probably mixtures of isomerides are formed.

TABLE VIII.

Isolation of cyclo*pentadienebenzoquinone.*

Solvent.	Initial concn. of reactants (mol./l.).	Volume (c.c.).	Time (hrs.)	Temp.	Yield, %.
C_6H_6	0·31	100	7	50°	94
EtOH	5·0*	180	24	20 – 30	92
	0·11	100	2·5	40	93

* Quinone not completely dissolved; concn. refers to total amount.

The velocity constants were calculated from the equations :

$$k = \frac{2\cdot30}{(t - t_0)C_\infty} \log_{10} \frac{\alpha(\alpha_0 - \alpha_\infty)}{\alpha_0(\alpha - \alpha_\infty)}$$

$$k = \frac{1}{at} \cdot \frac{\alpha_0 - \alpha}{\alpha - \alpha_0},$$

In both equations, α, α_0, and α_∞ represent the extinction coefficient at times t, 0, and infinity respectively; α_0' is the extinction coefficient of a *cyclo*pentadienebenzoquinone solution of the concentration a, and C_∞ is the quinone concentration for $t = \infty$.

In carrying out the rate measurements, the quinone solution was kept in a thermostat, and at zero time a *cyclo*pentadiene solution at the same temperature was introduced. The concentrations were so chosen that the volume after mixing differed by not more than 10—15% from the final volume after dilution to the mark. After some minutes the solution was transferred from the measuring flask to the absorption tube, also kept at the same temperature, and the absorption was continuously observed. A typical experiment is given below :

Solvent : alcohol. Thickness, 2·85 cm. Temp., 20·4°. Equimolar initial concentration, 0·0100 mol./l.

t (mins.)	0	26	35	45	56	72	85	101	∞
a (cm.$^{-1}$)	0·134	0·0951	0·0828	0·0744	0·0674	0·0581	0·0540	0·0477	0·001
k (l./g.-mol./min.)	—	1·7	1·9	1·9	1·7	1·9	1·9	1·9	—

The results of the kinetic measurements are in Table IX. When the mixture was equimolar only one concentration is given; otherwise, the initial concentration of *cyclo*pentadiene is added in brackets. For the constants k, the unit of concentration is g.-mol./l., and time is in mins. The means given in Table II are, however, calculated with the second as the unit of time. The specimens of solvents used (*a, b, c, d*) are shown in Table X. Some of the experiments were carried out in quartz cells, others in glass cells.

3 I

TABLE IX.

Results of kinetic measurements.

Solvent.	Temp.	Initial concn. (g.-mols./l.).	$C_6H_4O_2$ converted, %.	No. of obstns.	k (mean).
C_6H_6 (a)	20·4°	0·0500 *	75	4	0·43
	20·4	0·0200 *	60	6	0·40
	20·4	0·0200 [0·0100] *	82	4	0·39
	20·4	0·0100 *	75	5	0·40
	20·4	0·0200 †	50	4	0·42
	8·0	0·0200 †	30	4	0·15
	29·4	0·0100	60	4	0·87
	40·3	0·00500	55	3	2·1
	20·4	0·00200	53	4	0·39
C_6H_6 (b)	25·0	0·0200	55	3	0·53
EtOH (c) ‡	20·4	0·0100	70	8	1·8
	20·4	0·0100 [0·00330]	76	3	1·7
	20·4	0·00500	53	3	1·8
	20·4	0·00200	50	4	1·8
	2·3	0·0100	40	4	0·44
	11·2	0·0100	62	4	1·1
	21·0	0·00500	40	4	2·0
	30·0	0·00200	60	5	3·6
EtOH (d) ‡	39·0	0·00357	65	4	5·6

* The *cyclo*pentadiene solution used was not more than 10 mins old.
† The 0·04M-*cyclo*pentadiene solution was kept at 6° for 2 days before determination.
‡ Benzoquinone solutions freshly prepared before each determination.

TABLE X.

Velocity constants obtained with different specimens of solvents.

Benzene : (a) Merck's " zur Analyse ", (b) Specimen (a) dried for 6 months over Na_2SO_4, then 2 weeks over sodium, and distilled.

Ethyl alcohol : (c) Merck's " zur Analyse ", (d) " Absolute alcohol " (Burrough), kept for 3 months over CaO, then distilled Middle fraction, b p. 78·6°/756 mm.

	(a).	(b).	(c).	(d).
k (l /g.-mol /min.)	0·60	0·54	5·8	5·6
Temp.	25°	25°	39·0°	39·0°

The influence of light on the reaction was examined with an Osram " Nitra-Lamp " (220-volt, 500-watt). The filament was placed 35 cm. from the absorption tube containing 0·02M-mixtures in benzene at 20°. Experiments were also carried out with a Siemens quartz–cadmium lamp. First, 0·05M-solutions of benzoquinone were illuminated in quartz tubes, the windows of the air-bath (see *Nature, loc. cit.*, Fig. 1) also being of quartz. At 20° (layer thickness 2 cm.) in alcohol a marked darkening was observed after 60 mins. In benzene solution, however, no change could be detected after 180 mins.

In alcoholic solutions a slow discoloration is observed, even in the dark, but with the solutions (c) and (d) the reaction is so slow even at 40° that the kinetic mea surements were not disturbed. Mixtures (0·003—0·02M) of the reactants in benzene were illuminated with the cadmium lamp at 22—25° (thickness 3—4 cm.) for 200 mins. The image of the arc was projected into the vessel with a quartz condenser; experiments in diffuse light were also carried out. The effect of a magnetic field was examined at 20° in carbon tetrachloride solution with an electromagnet giving a field-intensity of 8900 gauss.

The experiments given in Table XI were carried out in the same way as those of Table IX. The substance added was first mixed with benzoquinone, and then the *cyclo*pentadiene solution was introduced. The comparison absorption tubes were filled with the solvent containing the added substance. It is possible that in Expt. No. 2 a part of the iodine was decolorised, the difference of the extinction coefficients (0·029 cm.⁻¹) being without significance. In No. 4 it was shown by titration that no measurable esterification of acid took place. Except for Expts. Nos. 5—7, no influence of the added substances on the colour of the quinone could be

found. In Nos. 5—7, the difference in the extinction coefficients after 10 mins. and 40 mins. was determined.

No.	....	—	5	6	7
Substance added	....	Nil	$FeCl_3$	$CuCl_2$	$MnCl_2$
$a_{10 mins.} - a_{40 mins.}$ (cm.$^{-1}$)	....	0·014	0·009	0·015	0·014

The pyridine in Expt. No. 14 was purified by way of its perchlorate.

TABLE XI.

Influence of added substances.

No.	Substance added.	Initial concn. of (I) and (II).	Mol of added substance per mol of $C_6H_4O_2$	Solvent.	Temp	Time (mins.).	a (cm.$^{-1}$) without added substance.	a (cm.$^{-1}$) with added substance.
1	I (dark)	0·0200	0·01	C_6H_6	25°	62	0·178	0·185
2	I (light)	0·0200	0·01	,,	25	64	0·176	0·147
3	aa'-Dipyridyl	0·0200	0·25	,,	25	133	0·141	0·143
4	p-$C_6H_4Me·SO_3H$	0·00500	16	EtOH	20	40	0·0484	0·0480
5	$FeCl_3$	0·00500	0·4	,,	20	—	—	—
6	$MnCl_2$	0·00500	0·4	,,	20	—	—	—
7	$CuCl_2$	0·00500	0·4	,,	20	—	—	—
8	trans-Stilbene	0·00500	0·4	,,	20	40	0·0484	0·0485
9	$CH_2I·CO_2H$	0·0200	0·5	C_6H_6	25	30	0·262	0·254
10	$CH_2Br·CO_2H$	0·0200	0·5	,,	25	30	0·262	0·244
11	$CH_2Cl·CO_2H$	0·0200	0·5	,,	25	30	0·262	0·228
12	PhOH	0·0200	1·3	,,	25	50	0·228	0·186
13	HCl	0·00500	0·5	EtOH	20	40	0·0484	0·0450
14	C_5H_5N	0·0200	1	C_6H_6	25	133	0·145	0·156

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191. *The Configuration of the Valencies of* 4-*Covalent Platinum : The Optical Resolution of* meso-*Stilbenediaminoisobutylenediaminoplatinous Salts.*

By WILLIAM H. MILLS and THOMAS H. H. QUIBELL.

ALTHOUGH the weight of evidence yielded by the many investigations carried out in recent years on the stereochemistry of the compounds of 4-covalent nickel, palladium, and platinum would seem to favour the view (first advanced by Werner for platinous compounds of the type [Pt a_2b_2]; *Z. anorg. Chem.*, 1893, **3**, 267) that the valencies of these elements in their 4-covalent state, instead of having the tetrahedral configuration usual in the compounds of 4-covalent elements, have a uniplanar arrangement, yet the question can scarcely be regarded as settled. We have therefore endeavoured to obtain evidence which would give a definite decision between the planar and the tetrahedral configuration of the valencies of platinum in one of the most stable types of the 4-co-ordination compounds of this element.

The compounds investigated were substitution derivatives of bisethylenediaminoplatinous salts, [en$_2$Pt]X$_2$. Although the frequency with which isomerism occurs in compounds containing a complex of the type [a_2Pt b_2] gives great weight to Werner's interpretation, yet it is always difficult, in dealing with geometrical isomerism, to make certain that the isomerism is actually of the nature supposed. There is no such difficulty with

mirror-image isomerism. We have accordingly studied the salts of a substituted bisethylenediaminoplatinum in which the substituents are so placed that the salts will possess molecular dissymmetry if the platinum covalencies lie in one plane, but must have symmetrical ions if these valencies have a regular tetrahedral arrangement (*i.e.*, if they have the relative directions of the four three-fold axes of the regular tetrahedron).

These substances were the diphenyldimethyl derivatives of bisethylenediaminoplatinous salts in which the substituents had the positions indicated in formula (IV), the two phenyl groups being in the *cis*-relationship.

$$
\text{(I.)} \quad
\begin{array}{l}
\text{CH}_2\cdot\text{NH}_2 \\
\text{CMe}_2\cdot\text{NH}_2
\end{array}
\xrightarrow{\text{K}_2\text{PtCl}_4}
\begin{array}{l}
\text{CH}_2\cdot\text{NH}_2 \\
\text{CMe}_2\cdot\text{NH}_2
\end{array}\!\!>\!\text{Pt}\!<\!\begin{array}{l}\text{Cl}\\\text{Cl}\end{array}
\quad \text{(II.)}
$$

$$
\text{(III.)} \quad
\begin{array}{l}
\text{PhCH}\cdot\text{NH}_2 \\
\text{PhCH}\cdot\text{NH}_2
\end{array}
\qquad\qquad
\left[\begin{array}{l}\text{CH}_2\cdot\text{NH}_2\\\text{CMe}_2\cdot\text{NH}_2\end{array}\!\!>\!\text{Pt}\!<\!\begin{array}{l}\text{NH}_2\cdot\text{CHPh}\\\text{NH}_2\cdot\text{CHPh}\end{array}\right]\text{Cl}_2
\quad \text{(IV.)}
$$
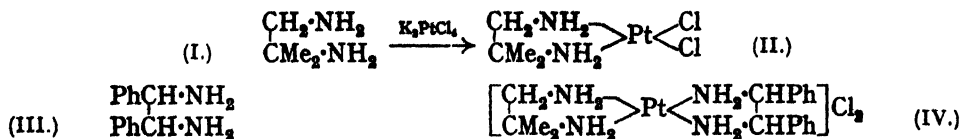
To obtain these salts iso*butylenediamine* (I) was treated with potassium chloroplatinite, and the resulting dimethylethylenediaminoplatinous chloride (II) (Drew and Head, J., 1934, 226) was made to interact with the *meso*-form of diphenylethylenediamine (stilbenediamine) (III).

The chelate base displaces (as chloride ions) the two chlorine atoms directly linked to the platinum, and occupies the co-ordination positions thus vacated, forming a salt (IV) of the required type.

It is evident that a cation of this structure will be dissymmetric if the platinum valencies lie in one plane, as shown in Fig. 1, but will possess a plane of symmetry if they have a tetrahedral arrangement, since the plane of symmetry of the diphenylated ring will then coincide with the plane of the dimethyl ring and become a plane of symmetry of the whole ion.

FIG. 1.
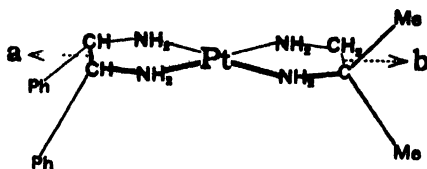
On investigation, these salts proved to be resolvable into antimeric optically active forms showing a high degree of optical stability.

The resolution was effected by means of diacetyltartaric acid. By fractional crystallisation of the *d*-diacetyltartrate the d-*diacetyltartrate* of the lævorotatory form of the platinum complex was isolated as the less soluble of the two diastereoisomeric salts. It showed $[M]_{5461} - 101°$ in water, the rotation due to the *d*-diacetyltartrate ion being $- 52°$. On conversion into iodide, a lævorotatory *iodide* [bn Pt sn]I$_2$ * with $[M]_{5461} - 68°$ in alcohol was obtained, and this, treated with silver chloride, gave the *chloride* [bn Pt sn]Cl$_2$, with $[M]_{5461} - 48.5°$ in water.

The platinum complex contained in the more soluble fractions of the *d*-diacetyltartrate was separated as *iodide* and converted into l-*diacetyltartrate*. By crystallisation of this, the *l*-diacetyltartrate of the *dextrorotatory* platinum complex was isolated ($[M]_{5461} + 103°$ in water) and from it the *dextrorotatory stilbenediamino*iso*butylenediaminoplatinous iodide* ($[M]_{5461} + 70.5°$ in alcohol) and the corresponding *dextrorotatory chloride* ($[M]_{5461} + 48.5°$ in water) were obtained.

The iodide and chloride crystallise with water of crystallisation, but there is no reason to doubt that the central platinum atom of the complex cation is truly 4-covalent; for, although the iodide is difficult to dehydrate completely, the chloride is readily obtained anhydrous, and the active chlorides retain their full optical activity after dehydration.

Also, a cryoscopic comparison of the chloride with barium chloride in aqueous solution showed that the two salts correspond closely in their cryoscopic behaviour, indicating that the platinum complex salt, like barium chloride, is unimolecular and at corresponding dilutions similarly dissociated into three ions.

The active salts have very considerable optical stability. In the cold no racemisation could be detected. Heated with dilute hydrochloric acid at 100°, a very slow loss of optical

* bn = iso*butylenediamine*; sn = *meso*-stilbenediamine.

activity takes place, but this may be due in part to interaction with the acid, since heating with concentrated hydrochloric acid was found to bring about the change

$$[\text{bn Pt sn}]Cl_2 + 2HCl = [\text{sn PtCl}_2] + \text{bn,2HCl.}$$
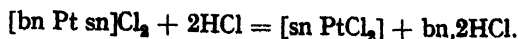
The complex salts are decomposed by reducing agents, such as magnesium or hydrazine, with the precipitation of metallic platinum and liberation of the co-ordinated bases.

The optically active chloride was treated in this manner, and after removal of the platinum, the resulting mixture of bases was found to be completely inactive. The diphenylethylenediamine thus liberated was extracted and found to be the pure inactive *meso*-form of the base (m. p. 119·5°). This observation removes any doubt there might be as to the actual optical inactivity of the bases co-ordinated with the platinum in the active salts. It proves that the dissymmetry of the molecule of the complex salt must arise from the relative positions in which the molecules of the two co-ordinated bases, themselves not dissymmetric, are held by the four co-valencies of the platinum atom.

With regard to the conclusions that may be drawn from the optical activity of these complex platinum salts, it is to be noted that, of the various possible arrangements of the four platinum covalencies, those which would give a *symmetrical* configuration for the cation of these salts (and are therefore excluded by the existence of the salts in antimeric optically active forms) are (1) the regular tetrahedral arrangement, and (2) all other arrangements in which the plane containing the two valencies linking the *iso*butylenediamine contains the line bisecting the angle between the two valencies linking the stilbenediamine and is at right angles to the plane of the latter valencies.

Dissymmetric configurations of the complex ion, on the other hand, would result from either (1) a planar arrangement, or (2) pyramidal, or (3) completely irregular tetrahedral arrangements, and any of these would accordingly be compatible with our observations.

Fig. 2.

Me   Me

Ph   Ph
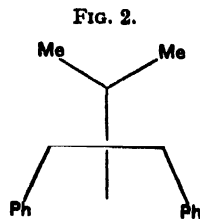
That the four platinum covalencies could have such an irregular tetrahedral arrangement as their normal configuration is, however, so improbable that it can safely be disregarded. It is also clearly impossible that the bisethylenediaminoplatinous ion, if regularly tetrahedral in its unsubstituted state, should undergo such distortion in consequence of the particular type of substitution we have employed as to produce a degree of molecular dissymmetry that would give rise to stable optical activity. This is apparent from the symmetrical disposition of the substituent groups in Fig. 2, which represents a projection of the tetrahedral ion on the plane perpendicular to the axis *ab* (Fig. 1).*

There are also no reasons for inferring a pyramidal rather than the more symmetrical planar configuration. A pyramidal configuration would lead to molecular dissymmetry in comparatively simple compounds, as, for example, in diammino*iso*butylenediaminoplatinous salts [bn Pt(NH₃)₂]X₂. The actual alternative configurations between which a decision is required are therefore the regular tetrahedral and the planar; and the stable optical activity of these diphenyldimethylbisethylenediaminoplatinous salts shows that, if these are the two alternatives, then the latter—the planar configuration—is that which the 4-covalent platinum atom must in fact possess.

In conclusion, it may be pointed out that cyclic systems in which, as in these platinum salts, one atom of the ring has a much greater diameter than the others present somewhat special stereochemical features.

If the valencies of 4-covalent platinum were tetrahedrally arranged, and consequently

* In a ring of symmetrical structure containing two *cis*-phenyl groups as vicinal substituents, the interaction between the phenyl groups will doubtless produce some distortion of the molecule in one direction or the other, in consequence of which it would exist, when at rest, in one of two antimeric equilibrium configurations. But the forces causing a distortion of this kind must be quite inadequate to prevent rapid inter-transformation from one configuration to the other through thermal agitation, so that optical activity stable at ordinary temperatures could not possibly arise from such a cause.

A parallel case exists in *cis*-hexahydrophthalic acid, which is well recognised to be incapable of existing in optically active forms (Werner and Conrad, *Ber.*, 1899, **32**, 3046).

had an intervalency angle of 109·5°, there would be very considerable interannular strain in a five-ring system composed of carbon and nitrogen atoms and one (4-covalent) platinum atom. On the other hand, the planar arrangement of the platinum valencies with the corresponding intervalency angle of 90° gives a practically strainless ring.

Fig. 3.
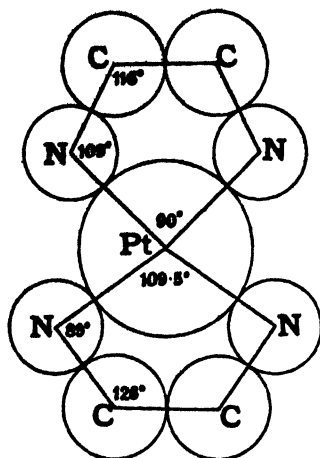
This is apparent from Fig. 3, which represents the ring atoms of the ethylenediaminoplatinum ring in the positions they assume (*a*) when the platinum intervalency angle is fixed at 90° (upper ring) and (*b*) at 109·5° (lower ring). For the atomic radii, the following values are taken : 4-covalent platinum 1·32 Å. (Pauling and Huggins, *Z. Krist.*, 1934, **87**, 205); carbon 0·77 Å.; nitrogen 0·70 Å.; and the resulting intervalency angles are indicated on the figure. Actually, of course, the strains would be distributed between the different atoms.

If the normal intervalency angles of carbon and ammonium nitrogen are taken as 109·5°, the average valency deflexion per atom amounts to 15° in the lower ring, but is only 3° in the upper ring.

These favourable stereochemical relationships of the five-membered ring with the planar platinum atom doubtless constitute one of the factors contributing to the stability of the ethylenediaminoplatinous compounds.

EXPERIMENTAL.

*iso*Butylenediamine.—The preparation of this base was first attempted by Ssidorenko (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 955), and subsequently it has been obtained, but incompletely described, by Reihlen, von Hessling, Hühn, and Weinbrenner (*Annalen*, 1932, **493**, 20), by Strack and Schwaneberg (*Ber.*, 1932, **65B**, 710), and by Drew and Head (J., 1934, 49). Catalytic reduction of α-acetamido*iso*butyronitrile was used by Reihlen, and of α-amino*iso*butyronitrile itself by Strack; Drew's method involved the reduction of α-amino*iso*butaldoxime. It has been found practicable to prepare *iso*butylenediamine by reduction of α-amino*iso*butyronitrile with sodium and alcohol, a method partially described by Strack and Fanselow (*Z. physiol. Chem.*, 1929, **180**, 159).

Dry ammonia is passed into crude acetone cyanohydrin (80 g.) in presence of anhydrous sodium sulphate (50 g.), the mixture being cooled at first in water. When the theoretical weight of ammonia is absorbed (about 4 hours), the liquid is decanted into 3 l. of fresh absolute alcohol and reduced by the rapid addition of 250 g. of sodium in 50-g. portions. The resulting mass is treated with water (600 c.c.) and distilled up to 100° in a vacuum, and the residue distilled in superheated steam at 140°. The distillates are collected in just sufficient dilute hydrochloric acid to keep the mixture acid, the alcohol removed and recovered, and the aqueous liquors evaporated to dryness on the water-bath. The yield of crude salt, which contains a little ammonium chloride, when dried in a vacuum over sulphuric acid, is usually 15—20 g. The dry salt is washed with alcohol, and boiled in concentrated aqueous solution with the gradual addition of 10% caustic soda until ammonia is removed. The hot, almost saturated solution is cautiously treated with an excess of 50% potash solution, and the upper layer of base separated and warmed with solid potash. The base is again separated from the aqueous potash layer and distilled from solid potash. The product is a colourless fuming oil, b. p. 112—115°/754 mm., 50°/21 mm., is hygroscopic, and approximates to the *monohydrate* in composition (Found : N, 25·0. $C_4H_{12}N_2,H_2O$ requires N, 26·3%).

The *anhydrous base*, prepared by the action of sodium on the hydrate and twice distilled from sodium in a vacuum, is an oil, b. p. 59°/20 mm., 62°/25 mm. (Found : C, 55·0; H, 13·7. $C_4H_{12}N_2$ requires C, 54·5; H, 13·7%).

The dihydrochloride was prepared from the base and dry hydrogen chloride in methyl-alcoholic solution, and dried in a vacuum. It forms small hygroscopic plates, which decompose at about 260° if heated slowly, and on rapid heating melt at 298—300° (decomp.). Strack (*loc. cit.*) gave m. p. 295° (Found : C, 29·9; H, 8·9; N, 17·2; Cl, 43·65. Calc. : C, 29·8; H, 8·8; N, 17·4; Cl, 44·0%).

The *dibenzoyl* derivative, after two crystallisations from aqueous alcohol, had m. p. 182° (Found : C, 72·9; H, 6·9; N, 9·4. $C_{18}H_{22}O_2N_2$ requires C, 72·9; H, 6·8; N, 9·5%).

meso-Stilbenediamine.—This base is prepared from amarin, either by Grossmann's method (*Ber.*, 1889, **22**, 2398) or, much more conveniently, by acetylation and hydrolysis of acetylamarin first to N-benzoyl-N'-acetylstilbenediamine, and then to *meso*-stilbenediamine itself.

Hydrobenzamide (100 g.) is heated in an oil-bath at 120—130° for 5 hours, and to the warm yellow product are added acetic anhydride (175 c.c.) and fused sodium acetate (3 g.), and the mixture boiled gently for 3 hours. The product is then treated with water (300 c.c.) and concentrated hydrochloric acid (25 c.c.) and heated for 2 hours on the water-bath. The precipitate is filtered off, well dried by means of the pump, and boiled out twice with 250 c.c. of spirit. The colourless solid is then dried at 100—120°. Yield, 54 g. (46%); m. p. 314—315°. On account of its marked insolubility in most solvents, benzoylacetylstilbenediamine is conveniently separated by boiling out soluble substances with alcohol. The pure substance is obtained by crystallisation from nitrobenzene, from which it separates in fine colourless needles; m. p. 316° (Japp and Moir, J., 1900, **77**, 611, gave 316°) (Found : C, 75·9; H, 6·2; N, 7·8. Calc. : C, 77·1; H, 6·2; N, 7·8%). The carbon determination was always low as stated by Japp and Moir.

54 G. of the crude benzoylacetylstilbenediamine are heated with water (550 c.c.) and concentrated sulphuric acid (550 c.c.) to boiling, and a current of steam passed to remove benzoic acid and prevent concentration of the sulphuric acid, which otherwise causes the production of yellow or brown colouring matter. After 2—3 hours, when hydrolysis is complete, the mixture is well cooled, and cautiously treated with ammonia and ice, the total volume being kept as small as possible. After the addition of 600 c.c. of ammonia (d 0·880), the mixture is left over-night, filtered through glass-wool to remove a sticky product, and made alkaline in the cold with excess (about 150 c.c.) of ammonia (d 0·880). The stilbenediamine separates in good yield and is almost colourless. It is crystallised several times from water, and forms colourless leaflets of m. p. 119·5° (uncorr.) (Japp and Moir gave m. p. 120°) (Found : C, 79·2; H, 7·55; N, 13·4. Calc. : C, 79·2; H, 7·6; N, 13·2%). The base is fairly soluble in hot water, only moderately in cold. On heating in air at 100°, it slowly develops a yellow colour.

Dichloroisobutylenediaminoplatinum (cf. Drew and Head, J., 1934, 226).—This was prepared by the action of *iso*butylenediamine on a slight excess of aqueous potassium platinochloride at the room temperature, and filtered off at intervals to avoid further action. It was thus almost free from the Magnus salt and formed yellow prisms in 64% yield. It decomposed without melting from about 263° upwards (Found : C, 13·5; H, 3·4; Cl, 20·0; Pt, 55·5. Calc. : C, 13·55; H, 3·4; Cl, 20·0; Pt, 55·1%).

dl-meso-*Stilbenediaminoisobutylenediaminoplatinous Iodide.*—19·5 G. of dichloro*iso*butylenediaminoplatinum are heated with *meso*-stilbenediamine (12 g.) in water (130 c.c.) to 100° for 5 hours, the mixture is then cooled and filtered, and warmed to about 30° whilst to it are added slowly with stirring 22 g. of sodium iodide dissolved in the least quantity of water. After some hours, the chilled mixture is filtered, and the precipitate washed with cold sodium iodide solution and a little water. The almost colourless complex *iodide* is obtained and dried at 100°. After recrystallisation from spirit, it forms colourless needles of the pure *monohydrate*; yield 19·4 g. The water is lost with difficulty even at 140°. The iodide has m. p. 269—270° (decomp.), and is sparingly soluble in cold water (Found : C, 28·1; H, 3·7; I, 33·05; Pt, 25·3. $C_{18}H_{28}N_4I_2Pt,H_2O$ requires C, 28·15; H, 3·9; I, 33·1; Pt, 25·4%).

dl-meso-*Stilbenediaminoisobutylenediaminoplatinous Chloride.*—The chloride is prepared by shaking the iodide (2·02 g.) in suspension in hot water (75 c.c.) with excess of freshly precipitated silver chloride. The liquid is decanted through an ordinary filter, and the residue extracted with a little boiling water. The filtrates are evaporated almost to dryness, the residue taken up in a little hot alcohol, and ether added to promote crystallisation. The yield of crystalline *chloride* is 1·37 g. (91%). Dried at 110°, it is anhydrous and has m. p. 291·5—292° (decomp.) (Found : C, 38·2; H, 5·0; Cl, 12·7; Pt, 33·9. $C_{18}H_{28}N_4Cl_2Pt$ requires C, 38·1; H, 5·0; Cl, 12·5; Pt, 34·5%). It is very soluble in water.

The d-α-*bromocamphor-π-sulphonate* was prepared from the iodide (3 g.) in boiling water (70 c.c.) and silver bromocamphorsulphonate (3·35 g.) in hot water (25 c.c.). After being heated for ¼ hour at 100°, the mixture was filtered, and the precipitate extracted with boiling water (50 c.c.). On concentration, the combined filtrates gave successive crops of fine colourless needles, apparently identical, and sparingly soluble in water, but rather more soluble in alcohol (Found : C, 39·8; H, 5·15; Pt, 17·3; loss at 145°, 2·2. $C_{38}H_{54}O_8N_4Br_2S_2Pt,1\frac{1}{2}H_2O$ requires C, 39·9; H, 5·2; Pt, 17·1; 1½H_2O, 2·4%).

The two extreme fractions from the aqueous liquor gave $[M]_{5461}$ = + 690° in 20% alcohol, and + 691° in 25% alcohol respectively, and no change of rotation was observed after 24 hours. Each fraction was precipitated from the aqueous alcohol as the insoluble picrate by means of aqueous sodium picrate, and the picrate filtered, washed and decomposed by dilute hydrochloric acid. After removal of the picric acid an inactive solution was obtained.

On crystallisation from alcohol the bromocamphorsulphonate afforded a homogeneous material giving $[M]_{5461}$ = + 700° in water, indicating no resolution.

The *picrate* is a yellow powder insoluble in water or alcohol, and when dried at 100° gave Pt, 20·5 ($C_{20}H_{22}O_{14}N_{10}Pt$ requires Pt, 20·5%).

The d-*camphor*-10-*sulphonate* was prepared from the iodide and an equivalent quantity of silver camphorsulphonate in aqueous solution. It is colourless and very soluble in water. The salt was crystallised six times from alcohol–ether, and dried at 100°. It crystallised easily and was apparently homogeneous (Found : C, 45·7; H, 6·1; Pt, 19·6. $C_{38}H_{58}O_8N_4S_2Pt,2H_2O$ requires C, 45·9; H, 6·3; Pt, 19·6%). 0·1444 G. in 20 c.c. of aqueous solution showed α = + 0·19°, $l = 2$, $\lambda = 5461$, or $[M]_{5461}^{18°}$ = + 135°, accounted for by the camphorsulphonate ions.

0·92 G. of this camphorsulphonate was precipitated in the cold by concentrated sodium iodide solution, but the iodide obtained was inactive in spirit.

The d-*tartrate* is best prepared from the soluble carbonate (obtained from the iodide and silver carbonate) by treatment in cold aqueous solution with the correct amount of tartaric acid. The solution is evaporated under reduced pressure at the ordinary temperature. The salt is very soluble in water and hot alcohol, and its solutions decompose gradually on heating or keeping. The salt obtained by evaporation at room temperature is the tetrahydrate (Found : Pt, 27·2. $C_{22}H_{32}O_6N_4Pt,4H_2O$ requires Pt, 27·3%). The salt dissolved in hot methyl alcohol but separated after a minute as the *monohydrate* in a fine powder, which was dried at the ordinary temperature (Found : C, 39·6; H, 5·6; N, 8·4; Pt, 29·4. $C_{22}H_{32}O_6N_4Pt,H_2O$ requires C, 39·9; H, 5·2; N, 8·5; Pt, 29·5%). This crystallised slowly in very small crystals from aqueous methyl alcohol on the addition of acetone. The product was converted into the iodide, which proved to be inactive in alcohol.

The diacetyl-d-tartrate. 25 G. of iodide (m. p. 269—270°), suspended in 250 c.c. of warm water, were well shaken for an hour with freshly precipitated silver carbonate from 15 g. of silver nitrate, and the mixture filtered first at the pump, then through an ordinary filter to remove finely divided silver salts. To the filtrate were added 7·25 g. of diacetyltartaric anhydride (Chattaway and Parkes, J., 1923, 123, 663), and the whole was evaporated in a vacuum below 60° as rapidly as possible to avoid hydrolysis. The products from four such preparations were mixed and crystallised. The only satisfactory procedure was to dissolve the salt (10 g.) in a very little warm water (6 c.c.) and to add a large excess (200 c.c.) of absolute (99%) alcohol. The salt separates slowly and is filtered after 24 hours, and dried in a vacuum over sulphuric acid after each crystallisation. It is hygroscopic, exceedingly soluble in water, and hydrated. Dried at 100°, it approximates to the dihydrate.

After seven crystallisations thus from aqueous alcohol, a less soluble fraction consisting of well-formed colourless plates was obtained, which after drying in a vacuum at 85° gave $[\alpha]_{5461}$ = − 13·9° in water. After two further crystallisations $[\alpha]_{5461}$ was − 13·6°.

By systematic fractionation, 16·4 g. of l-meso-*stilbenediaminoisobutylenediaminoplatinous diacetyltartrate* (Found : C, 41·9; H, 5·2; Pt, 26·1. $C_{26}H_{36}O_8N_4Pt,H_2O$ requires C, 41·8; H, 5·1; Pt, 26·2%) were obtained from the initial 100 g. of racemic iodide. The substance when vacuum-dried at 85° discolours from about 245° and melts with rapid decomposition at 275°. 0·2535 G. in 30 c.c. of aqueous solution at 16° gave α = − 0·46° ($l = 4$), $\lambda = 5461$, whence $[\alpha]_{5461}^{16°}$ = − 13·6°, $[M]_{5461}^{16°}$ = − 101°. Attempts to dry the salt at temperatures above 100° led to gradual decomposition.

For comparison, the rotation of the d-diacetyltartrate ion was found by observations on disodium diacetyltartrate in similar conditions to be $[M]_{5461}$ = − 52° approximately, indicating therefore a rotation for the complex platinum ion of about − 49°.

2·2743 G. of diacetyltartaric anhydride and 1·7683 g. of sodium bicarbonate were each dissolved in cold water, mixed, well shaken until evolution of carbon dioxide ceased, and made up to 100 c.c., the total concentration being equal to 2·928 g. of disodium salt in 100 c.c. The solution, with $l = 4$, $\lambda = 5461$, at 20°, gave α = − 2·11°; diluted to half strength, α = − 1·08°, and diluted to ¼ strength, α = − 0·38°. The corresponding values of [α] are − 18·0°, − 18·4°, − 19·4°; and of [M] − 50°, − 51°, − 54°.

l-meso-*Stilbenediaminoisobutylenediaminoplatinous Iodide.*—To 8·47 g. of the *l*-complex

diacetyltartrate dissolved in water (20 c.c.) was slowly added a solution of sodium iodide (5 g.) in water (9 c.c.). The complex iodide crystallised, and was filtered off, washed with 20% sodium iodide solution followed by acetone, and dried at 100°.

The l-*iodide* is sparingly soluble in water but more soluble in alcohol; 0·2995 g. in 30 c.c. of alcoholic solution, at 17°, $\lambda = 5461$, gave $\alpha = -0.355°$, $l = 4$, or $[M]_{5461}^{17°} = -68°$. After one crystallisation from spirit, 7·14 g. of colourless, long, thin prisms were obtained. These, when dried at 100°, had m. p. 271—272° (decomp.) (Found : C, 28·6; H, 3·9; N, 7·3; I, 33·1; Pt, 25·25; loss at 85° in a vacuum, 1·7. $C_{18}H_{28}N_4I_2Pt,H_2O$ requires C, 28·2; H, 3·9; N, 7·3; I, 33·1; Pt, 25·4; H_2O, 2·3%). 0·358 G. in 30 c.c. of alcoholic solution gave $\alpha = -0.42°$, $l = 4$, at 19°, $\lambda = 5461$, whence $[M]_{5461}^{19°} = -68°$. The rotation remained constant.

l-meso-*Stilbenediaminoisobutylenediaminoplatinous Chloride.*—4 G. of the iodide suspended in water (75 c.c.) at 40° were shaken with an excess of freshly precipitated silver chloride for 2 hours. The silver halides were filtered off and washed with 20 c.c. of hot water, and the solution evaporated rapidly on the water-bath until crystallisation set in. The mass was taken up in hot spirit (30 c.c.), filtered from traces of silver halide, and caused to crystallise by the addition of ether. The l-*chloride* crystallises as the *dihydrate* in clusters of colourless fine silky needles; yield 3·13 g. (almost theoretical) (Found : Cl, 11·8; Pt, 32·3. $C_{18}H_{28}N_4Cl_2Pt,2H_2O$ requires Cl, 11·8; Pt, 32·4%).

The water is lost at 100° or in a vacuum at 90°. For polarisation and analysis, the salt was dried for 3 hours at 90° in a vacuum. It discolours at 290—291°, and melts at 295° (decomp.) (Found : C, 37·9; H, 5·1; N, 9·8; Cl, 12·5; Pt, 34·2. $C_{18}H_{28}N_4Cl_2Pt$ requires C, 38·1; H, 5·0; N, 9·9; Cl, 12·5; Pt, 34·5%).

1·0038 G. in 30 c.c. of aqueous solution ($l = 4$) at 18° gave : $\alpha = -1.03°$, $\lambda = 5780$, $[M]_{5780} = -43.5°$; $\alpha = -1.15°$, $\lambda = 5461$, $[M]_{5461} = -48.5°$; $\alpha = -1.88°$, $\lambda = 4359$, $[M]_{4359} = -79.7°$.

0·5 G. of the chloride ($[M]_{5461} = -48.5°$) in water (25 c.c.) was heated on the water-bath for 2 hours with 50% hydrazine hydrate (4 c.c.) and sodium hydroxide (0·3 g.). After acidification with acetic acid and removal of the precipitated platinum, the solution, made up to 30 c.c., was found to be optically inactive. On making it alkaline, meso-stilbenediamine (0·144 g.; 77% of theory) crystallised with m. p. 119—119·5°; mixed m. p. with authentic meso-stilbenediamine, 119—119·5° (Found : C, 79·4; H, 7·8. Calc. : C, 79·2; H, 7·6%).

In a comparison by the freezing-point method with barium chloride, the results in the same conditions were :

Barium chloride.			l-Complex chloride.		
G.-mols./1000 g. H_2O.	Measured depression.	Molecular depression.	G.-mols./1000 g. H_2O.	Measured depression.	Molecular depression.
0·01617	0·088°	5·44°	0·0327	0·192°	5·88°
0·03678	0·192	5·22	0·0389	0·200	5·27
0·09677	0·495	5·12	0·0692	0·343	4·95
0·1439	0·727	5·05			
	Mean	5·2		Mean	5·4

Hall and Harkins (*J. Amer. Chem. Soc.*, 1916, **38**, 2674) found 5·08° and 4·70° for concentrations of 0·01 and 0·1 g.-mol. of barium chloride per 1000 g. of water respectively.

The chloride values thus correspond with those for barium chloride, indicating that the complex chloride is a monomeric ternary electrolyte.

d-meso-*Stilbenediaminoisobutylenediaminoplatinous Diacetyl-l-tartrate.*—The more soluble fractions of the diacetyl-*d*-tartrate which were found polarimetrically to contain an appreciable excess of the *d*-complex *d*-acetyltartrate were reconverted into the iodide, and the iodide converted by way of the carbonate and diacetyl-*l*-tartaric anhydride into the diacetyl-*l*-tartrate.

20·5 G. of this iodide furnished diacetyltartrate, from which, after four crystallisations as described, were isolated 10·2 g. of pure *d*-complex *diacetyltartrate*. This was dried in a vacuum at 90°, and showed m. p. 275° (decomp.), after previous discoloration. The salt forms colourless hygroscopic plates and is the monohydrate (Found : C, 41·6; H, 5·4; Pt, 26·0. $C_{26}H_{36}O_8N_4Pt,H_2O$ requires C, 41·8; H, 5·1; Pt, 26·2%). 0·2014 G. in 30 c.c. of aqueous solution gave $\alpha_{5461} = +0.37°$ ($l = 4$), at 20°, or $[\alpha]_{5461}^{20°} = +13.9°$, $[M]_{5461}^{20°} = 103°$.

The d-*iodide.* 8·1 G. of the above diacetyltartrate were converted into the iodide by the method used for the *l*-series, and the *d*-iodide was crystallised from spirit and dried at 100°. Yield, 7·15 g. of colourless long flat prisms, which discolour at about 255° and melt at 270—272° (rapid decomp.). The *monohydrate* is thus obtained (Found : C, 28·3; H, 3·8; N, 7·3;

I, 33·2; Pt, 25·4; loss in vacuum at 115°, 2·2. $C_{18}H_{28}N_4I_2Pt,H_2O$ requires C, 29·2; H, 3·9; N, 7·3; I, 33·1; Pt, 25·4; H_2O, 2·3%). The *anhydrous* salt gave I, 34·1 ($C_{18}H_{28}N_4I_2Pt$ requires I, 33·9%).

An alcoholic solution of 0·3630 g. of the monohydrate in 30 c.c. gave $\alpha_{5461} = + 0·445°$ at 19° ($l = 4$), whence $[M]^{19°}_{5461} = + 70·5°$. The rotation was constant.

The d-chloride. 4 G. of the *d*-iodide monohydrate were converted by means of silver chloride into the chloride, and this crystallised from alcohol with the addition of ether. Yield, 3·03 g. (97%) of the *dihydrate* in clusters of colourless, fine, silky needles (Found : Cl, 11·7; loss in a vacuum at 90°, 6·1. $C_{18}H_{28}N_4Cl_2Pt,2H_2O$ requires Cl, 11·8; $2H_2O$, 6·0%).

The *anhydrous* salt was prepared from the hydrate by drying for 3 hours at 90° in a vacuum (Found : C, 38·1; H, 5·0; Cl, 12·4; Pt, 34·6. $C_{18}H_{28}N_4Cl_2Pt$ requires C, 38·1; H, 5·0; Cl, 12·5; Pt, 34·5%). It discolours at 290—291° and melts at 295° (decomp.).

1·0006 G. of this anhydrous chloride were made up to 30 c.c. in water at 19° and gave ($l = 4$) : $\alpha = + 1·01°$, $\lambda = 5780$, $[M]_{5780} = + 42·7°$; $\alpha = + 1·14°$, $\lambda = 5461$, $[M]_{5461} = + 48·5°$; $\alpha = + 1·90°$, $\lambda = 4359$, $[M]_{4359} = + 81·2°$.

The rotation was stable in aqueous solution. The solution (total volume 32 c.c.) was then heated with 3·5 c.c. of 10N-hydrochloric acid for 1¼ hours at 100°, being allowed to concentrate to just less than 30 c.c. After being made up to 30 c.c. again, it had $\alpha_{5461} + 1·12°$, a reduction of only 2%. After 4 hours' heating, the solution being allowed to concentrate to about 7 c.c., 0·025 g. of yellow crystals separated. The filtrate, made up to 30 c.c., gave $\alpha_{5461} = + 0·92°$; hence 82% of the activity persists. The yellow substance, washed with hot alcohol and ether, proved to be *dichlorostilbenediaminoplatinum* (Found : Pt, 40·8. $C_{14}H_{16}N_2Cl_2Pt$ requires Pt, 40·8%).

Melting-point determinations indicate the formation of a racemic compound between the *d*- and the *l*-complex chloride. Parallel determinations of m. p.'s gave the following results : *d*-chloride, 295°; 71·5% *d* + 28·5% *l*, 287·5—288·5°; racemic chloride, 291·5—292°; 31% *d* + 69% *l*, 284—285°; *l*-chloride, 295°.

l-Diacetyltartaric Anhydride.—*l*-Tartaric acid, from ammonium *l*-tartrate (Kellett, *J. Soc. Chem. Ind.*, 1932, **51**, 204), was acetylated by heating with acetic anhydride and two drops of concentrated sulphuric acid at 80° for a few minutes, and on scratching, the acetyltartaric anhydride separated. It was filtered off, washed with acetic anhydride, and dried in a vacuum over potash. It was recrystallised from dry benzene containing a little acetic anhydride, washed with dry ether, and dried in a vacuum. It forms long needles, m. p. 133·5—135°, and is very deliquescent, absorbing moisture from the air even at 100° (Found : C, 44·5; H, 4·2. $C_8H_8O_7$ requires C, 44·4; H, 3·7%).

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192. *An X-Ray Study of the Hydration and Denaturation of Proteins.**

By W. T. ASTBURY and R. LOMAX.

COMPARATIVE studies of the *X*-ray photographs given by proteins (Astbury, *Trans. Faraday Soc.*, 1933, **29**, 193; Cold Spring Harbor Symposia on Quantitative Biology, 1934, **2**, 15; *Kolloid-Z.*, 1934, **69**, 340), in particular of the " fibre photographs " given by the keratin of mammalian hairs (Astbury, *Ann. Reports*, 1931, **28**; Astbury and Street, *Phil. Trans.*, 1931, *A*, **230**, 75; Astbury and Woods, *ibid.*, 1933, **232**, 333), lead to the conclusion that a fully extended polypeptide chain is characterised by two principal side-spacings approximately at right angles to each other, one (about 4½ Å.) arising from the effective thickness of the " backbone " of the chain, and the other (about 10 Å.) from the average lateral extension of the side-chains standing out from the amino-acid residues. These

two spacings thus appear to represent the two principal modes of linkage of neighbouring protein chains : they may be illustrated, purely diagrammatically, by Figs. 1*a* and 1*b*.

The identification of the side-chain spacing rests largely on the results of the X-ray examination of the interaction of proteins with water, *e.g.*, the action of steam, hot water, or cold dilute caustic alkali on β-keratin (stretched hair), where it can be shown geometrically that the reaction is associated almost exclusively with a disturbance in the longer side-spacing (9·8 Å.). Collagen, gelatin, and related structures show analogous well-marked changes simply on wetting, and in this case there is a continuous increase in the side-chain spacing as the water penetrates between the molecular chains. Figs. 2*a* and 2*b*, respectively, show the action of steam on β-keratin and the action of cold water on elastoidin fibres * from a fin of *Carcharias*. In Fig. 2*a* certain reflexions are drawn out along the hyperbolic " layer-lines," and the distribution of these elongated spots (which present a normal

FIG. 1.
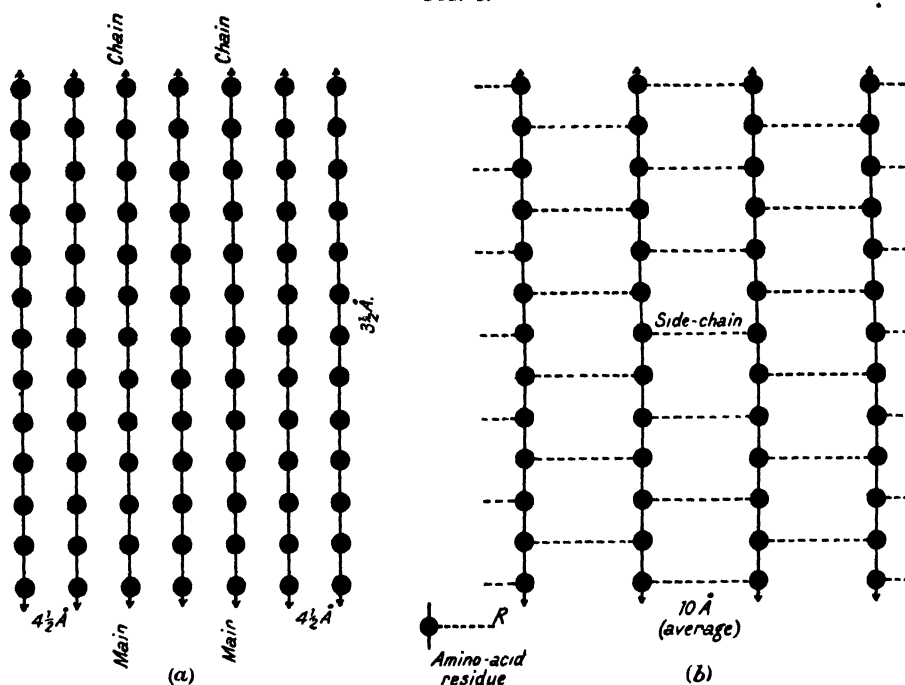
The two principal modes of linkage of neighbouring protein chains : (a) " backbone " linkage : (b) side-chain linkage.

appearance in X-ray photographs of untreated β-keratin) indicates that there has occurred, on steaming, a unidirectional disturbance parallel to the larger side-spacing. Fig. 2*b* is a double photograph taken on one film, the top half being of elastoidin fibres after drying over phosphoric oxide, and the bottom half after wetting with water. It will be seen that the equatorial reflexion nearest the centre (the side-chain reflexion) is displaced and drawn out towards the centre of the photograph by the action of the water.

Most proteins, however, as ordinarily available, do not give clear-cut crystal effects, but only diffuse ring photographs showing little more than what appear to be the back-bone and side-chain spacings of polypeptide chains. It is important, therefore, to test this conclusion also by swelling reactions, and to this end a number of non-fibrous proteins were photographed both dry and after adsorption of water or alcohol. The proteins examined were : ordinary egg-white, boiled egg-white, serum albumin, serum albumin

* For these fibres we are indebted to Prof. W. J. Schmidt, of Giessen (see Schmidt, " Polarisations-optische Analyse des submikroskopischen Baues von Zellen und Geweben," p. 601, in Abderhalden's " Handbuch der biologischen Arbeitsmethoden," 1934).

denatured by heat, pepsin,* trypsin,* zein,† commercial casein, tobacco-seed globulin, squash-seed globulin, and edestin from hemp seed : X-ray photographs of eight of these at ordinary humidity are shown in Figs. 3, (1)—(8). For the purposes of the discussion given below they are arranged in descending order of " crystallinity "; *i.e.*, as we proceed from (1) to (8), the X-ray reflexions become both fewer and more diffuse.

All the photographs were taken with Cu-K_α rays, the protein being packed into a small hole drilled through a microscope slide. The camera was in the form of a closed box in which the specimen could be kept wet or (except just below saturation) at approximately constant humidity at laboratory temperature. In front of the photographic film was a metal slider by means of which first one half of the film, and then the other, could be protected from the diffracted X-rays. In this way, two comparable photographs could be taken on one and the same film without disturbing the adjustment of either specimen or film—the latter, of course, was carefully shut off from the effects of the various humidity changes.

Figs. 4, (1)—(10), show the double photographs so obtained of ten proteins, the left half always being that of the specimen after drying for about 2 days over phosphoric oxide, and the right half after exposure to water or alcohol vapour or actual wetting with water.

Both the ordinary and boiled egg-white were first dried over phosphoric oxide, and then allowed to take up the humidity required. The serum albumin was denatured by gently heating a solution in distilled water till precipitation occurred.

FIG. 2*a*.

X-Ray fibre photograph of human hair stretched in steam to double its initial length (" steam-set " β-keratin).

FIG. 2*b*.

Comparable X-ray fibre photographs of dry (top) and wet (bottom) elastoidin fibres from a fin of Carcharias.

FIG. 3.

X-Ray powder photographs of proteins at atmospheric humidity : (1) Tobacco-seed globulin, (2) squash-seed globulin, (3) edestin from hemp seed, (4) boiled egg-white, (5) pepsin, (6) ordinary egg-white, (7) casein, (8) zein.

FIG. 4.

X-Ray powder photographs of proteins after being dried over phosphoric oxide (left), and then exposed to water or alcohol vapour or wetting with water. (1) Ordinary egg-white, dry and at 100% relative humidity ; (2) boiled egg-white, dry and at 100% relative humidity ; (3) serum albumin, dry and at 100% relative humidity ; (4) denatured serum albumin, dry and at 100% relative humidity ; (5) trypsin, dry and at 90% relative humidity (plus ammonium sulphate) ; (6) zein, dry and wet with water ; (7) zein, dry and in alcohol vapour ; (8) squash-seed globulin, dry and wet with water ; (9) squash-seed globulin, dry and in alcohol vapour ; (10) pepsin, dry and wet with water (second effect).

FIG. 5.

X-Ray powder photographs of normal and denatured albumins at atmospheric humidity : A_1, normal egg white ; B_1, normal serum albumin ; A_2, boiled egg white ; B_2, heat-denatured serum albumin.

DISCUSSION.

Protein Powder Photographs.—Fig. 3 illustrates well the general similarity between X-ray powder photographs of proteins as ordinarily available : in every case the diffraction pattern either consists solely of, or is based on, a pair of rings of roughly constant dimensions, and, as pointed out above, existing evidence suggests strongly that the inner ring is to be associated with the side-chain spacing, and the outer with the backbone spacing, of polypeptide chains.

The table gives the spacings of the various rings shown by the photographs of Fig. 3. It will be apparent that the backbone spacing is much more constant than the side-chain spacing—the former has a mean variation of less than 0·1 Å. about its mean ($4·5_9$ Å.), whereas the latter has a mean variation of more than 0·5 Å. about its mean ($10·4_2$ Å.). This in itself provides a sound argument in favour of the proposed interpretation of the two spacings, for, although we should indeed expect the average side-chain separation of poly-

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* Kindly sent by Prof. J. H. Northrop (see *J. Gen. Physiol.*, 1930, **13**, 739; 1932, **16**, 267).

† Both commercial zein and a preparation by Prof. A. C. Chibnall.
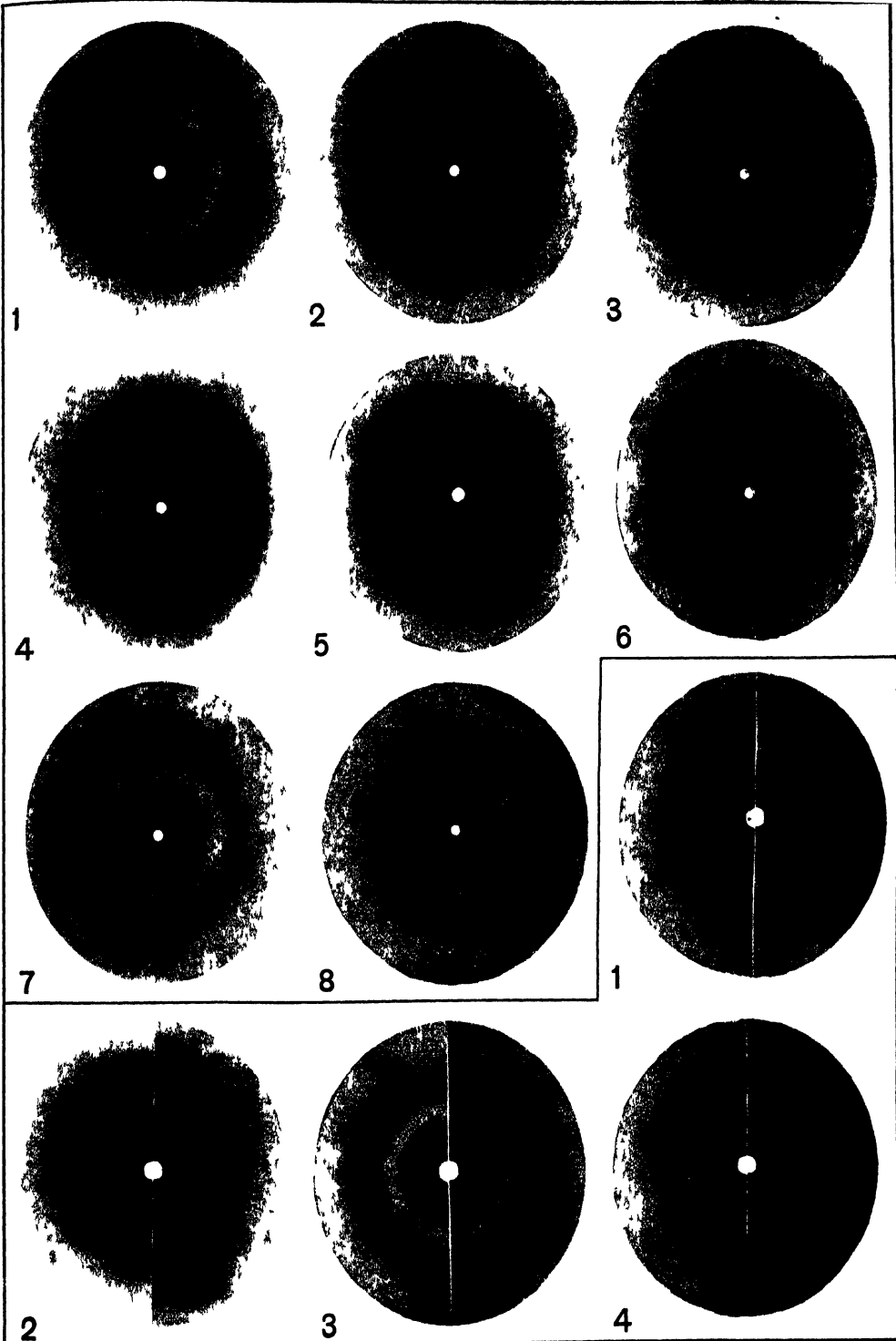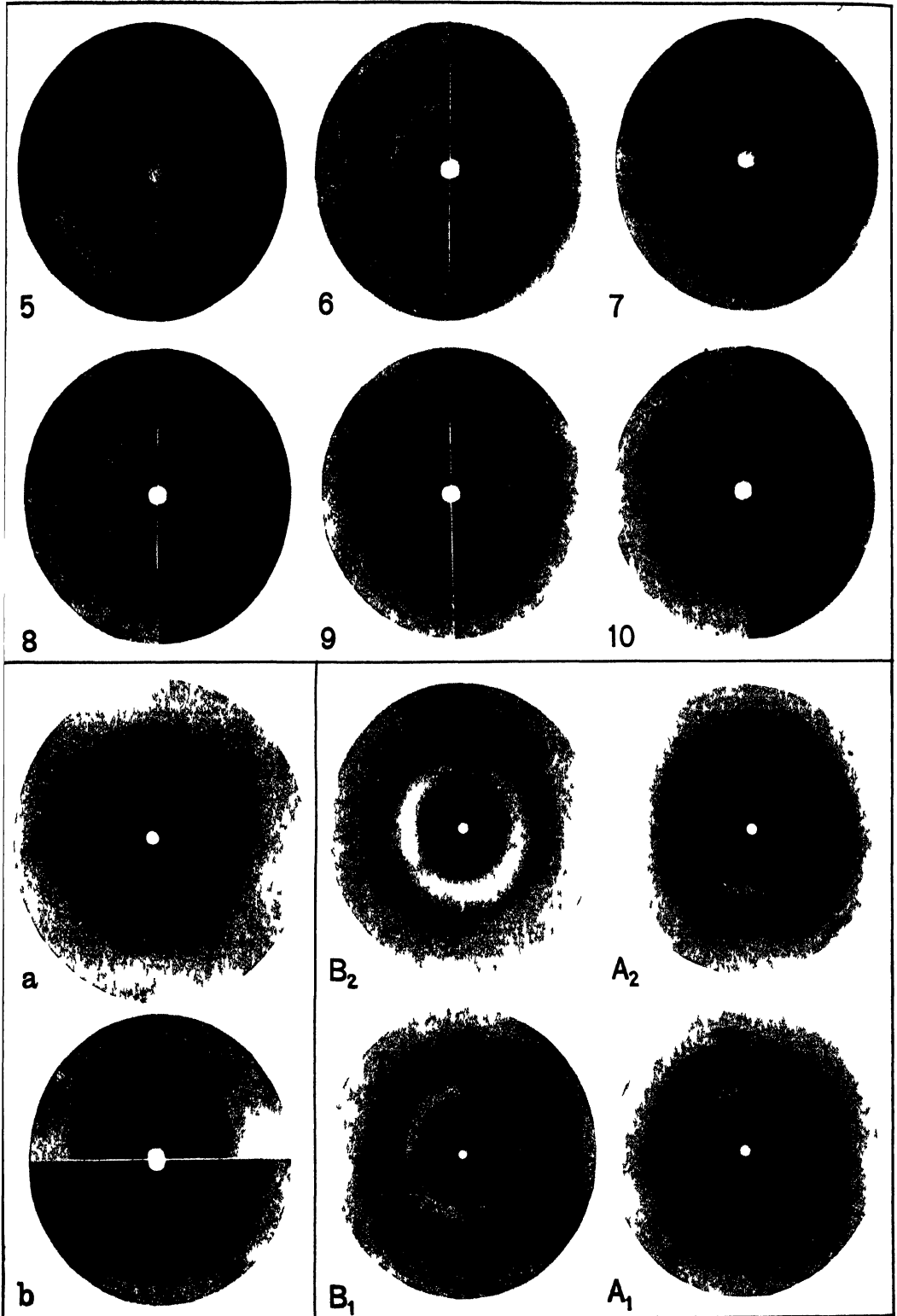
FIG 3

FIG 4

[*To face p.* 848.

FIG 4

peptide chains to be always roughly of the same order, yet we might expect the backbone separation to be almost constant. The backbone linkage should to a certain extent be independent of the nature of the side-chains if the main-chains are fully extended, a reasonable scheme of inter-chain attractions being the following (Astbury and Woods, *loc. cit.*; *Nature*, 1931, **127**, 663; Lloyd, *J. Soc. Chem. Ind.*, 1932, **51**, 141 T):

About 4½ Å.
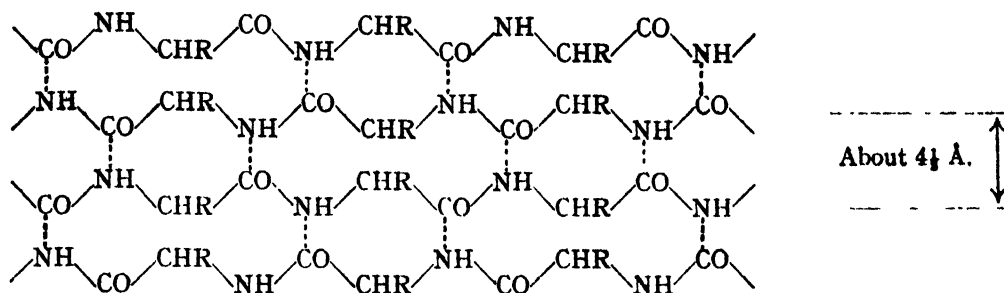
[N.B. The side-chains (R-groups) must be thought of as standing out above and below the plane of the paper.]

Spacings (Å.U.) *in* X-*ray powder photographs of proteins at ordinary humidity.*

(S = Side-chain spacing; B = backbone spacing.)

	S.					B.			
Tobacco-seed globulin	$11 \cdot 0$	$8 \cdot 6_4$	$7 \cdot 1_3$	—	$4 \cdot 9_9$	$4 \cdot 4_3$	$3 \cdot 9_5$	$3 \cdot 5_7$	$3 \cdot 1_7$
Squash-seed globulin	$11 \cdot 0_6$	$8 \cdot 9_5$	$7 \cdot 2_5$	$5 \cdot 7_3$	$5 \cdot 1_4$	$4 \cdot 4_5$	$3 \cdot 9_8$	$3 \cdot 6_3$	$3 \cdot 2$
Edestin	$11 \cdot 0$	—	—	—	—	$4 \cdot 5_5$	—	$3 \cdot 6$	—
Pepsin	$11 \cdot 5$	—	$6 \cdot 5_5$	--	—	$4 \cdot 5_9$	--	$3 \cdot 6$	—
Denatured egg albumin	$10 \cdot 2_3$	—	--	—	--	$4 \cdot 7_5$	--	$3 \cdot 6_7$	—
Denatured serum albumin	$9 \cdot 6$	—	—	—	—	$4 \cdot 4_8$	--	$3 \cdot 6$	—
Egg albumin	$10 \cdot 6_5$	-	—	--	—	$4 \cdot 7_5$	—	—	--
Serum albumin	$9 \cdot 7_1$	-	—	—	—	$4 \cdot 5_9$	—	—	—
Zein	$9 \cdot 8_2$	--	—	—	—	$4 \cdot 6_4$	—	—	—
Casein	$10 \cdot 2_3$	—	—	--	—	$4 \cdot 5_9$	—	—	—
Trypsin	$9 \cdot 8_2$	—	—	—	—	?	—	—	—

The Penetration of Water and Alcohol.—Turning now to the double photographs of Fig. 4, it will be seen that in every case where spacing changes occur on adsorption of water or alcohol vapour, it is the postulated side-chain spacing that increases most, just as expected : the backbone spacing always remains unchanged, or nearly so. Considerable increases are observed in the side-chain spacings of the albumins on exposure to water vapour, and also when zein is exposed to alcohol vapour; but the seed globulins appear to be unaffected by alcohol vapour, and only slightly so by water vapour. The effects shown by pepsin are complex. When first received, the specimen showed also a marked increase in the side-chain spacing on wetting; but on re-examination some months later it was found that wetting produced a new photograph [Fig. 4 (10), right-hand side] which yet always reverted to the original (left-hand side) on drying. In this second photograph of wet pepsin the two main rings are replaced each by a pair of sharper rings.

These swelling results, then, like the spacing measurements quoted above, pronounce definitely in favour of the hypothesis under investigation.

Protein Denaturation (cf., *e.g.*, Lloyd, " Chemistry of the Proteins," 1926, Chap. XIII).— Fig. 5 shows for close comparison the X-ray powder photographs of the albumins before and after denaturation by heat. The change accompanying denaturation is simply a sharpening of the backbone reflexion and the appearance of at least one other outer ring of spacing about 3·6 Å. (cf. table) : *i.e.*, denaturation of the albumins merely moves them higher up in the " crystallinity series " represented by the photographs of Fig. 3. All these photographs seem to be based on a common structural scheme; in fact, they all appear to arise from crystallites built of parallel, fully-extended polypeptide chains, between which the principal cross-linkages are as illustrated in Fig. 1. Denaturation, then, results in a well-marked improvement in, or development of, this particular mode

of regular aggregation, which is faintly envisaged even in the " poorest " protein photographs, such as those of casein and zein. Before denaturation, the peptide chains of the protein molecule seem to be clinging together chiefly by way of their side-chains, as might be expected (Fig. 1b); but after denaturation, this interaction is consolidated by marked coalescence of the main-chains by way of the backbone linkage also (Fig. 1a), as is shown clearly by the sharpening of the corresponding X-ray reflexion and the appearance of at least one new reflexion.[*]

To appreciate this result in its proper perspective, it is necessary to consider once more the series of photographs shown in Fig. 3, and to ask ourselves what property, or properties, the proteins there represented have in common. They include obviously very different proteins covering a range of molecular weights, as determined by the ultra-centrifuge, from 34,500 to about 200,000 (see, *inter alia*, Krejci and Svedberg, *J. Amer. Chem. Soc.*, 1934, **56**, 1706), yet they all appear, in varying degrees, to be in a state of similar molecular aggregation—in fact, that state which actually " crystallises out," so to speak, when the albumins are deliberately denatured by heat. The answer to the question must be in three parts as follows : (i) all the proteins photographed are peptides 'or combinations of peptides; (ii) increasingly marked crystallinity of the type shown in Fig. 3 is an expression of increasingly marked degeneration or denaturation; and (iii) the completely denatured state is that in which the peptide chains have been freed from any specific configuration and aggregated into regular bundles, or crystallites, held together by two principal linkages, the backbone and side-chain linkages illustrated above.

There does not appear to be any difficulty, in view of the source and age of the proteins examined, and also of the fact that they had all been dried, in accepting the argument that they must have been in various stages of degeneration or denaturation : the results presented here can hardly be interpreted in any other way. Only one protein, pepsin, has as yet been analysed by X-rays while in the truly active crystalline state (Bernal and Crowfoot, *Nature*, 1934, **133**, 794),[†] and the photographs obtained are totally different from the pepsin photographs shown in Figs. 3 and 4 (Astbury and Lomax, *ibid.*, p. 795). Indeed, the former are apparently photographs of a regular array of more or less *globular* molecules, in agreement with the molecular shape deduced from the results of experiments with Svedberg's ultracentrifuge (Philpot and Eriksson-Quensel, *ibid.*, 1933, **132**, 932).

From this point of view, the fibrous proteins, such as fibroin, gelatin, keratin, and myosin (Boehm and Weber, *Kolloid-Z.*, 1932, **61**, 269; Astbury and Dickinson, *Nature*, 1935, **135**, 95), may all be looked upon as either actually in a state of denaturation, or configurationally disposed towards such a state. Fibroin and keratin are very insoluble proteins, and so is myosin when once it has been thoroughly dried, and even gelatin becomes progressively more insoluble on standing. At all events, we appear to have a significant analogy between these characteristically stable proteins and non-fibrous proteins which have been brought into a stable and resistant state by one or other of the methods of denaturation. One of the simplest of these methods is the act of dehydration—*e.g.*, the globulins are susceptible in this way, while most so-called protein " crystals " in the dry state are probably only pseudomorphs after partial or complete denaturation—and here, at least, the elastic properties of keratin (Astbury and Woods, *loc. cit.*) suggest an interpretation. The intramolecular transformation from α- to β-keratin, or the reverse, is inhibited in the absence of water, for the reason that, unless the active side-chains are solvated, they seize upon one another so strongly that the possibility of intramolecular movement is practically eliminated. Similar ideas also account satisfactorily for the well-known hysteresis between the adsorption and desorption of water by proteins, while for stability to be maintained in regular aggregations (crystals) of " globular " protein molecules we can imagine that it is essential for each molecule to be " protected " from its

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[*] The side-chain reflexion being called (001) and the backbone reflexion (200), as in β-keratin (Astbury and Street, *loc. cit.*), this reflexion of spacing about 3·6 Å. would appear to correspond to (210), perhaps slightly confused with (020).

[†] [Note added in proof.] Crystalline insulin has now been analysed, and similar conclusions drawn (Crowfoot, *Nature*, 1935, **135**, 591).

neighbours by an intermolecular wrapping of water or some still more specific reagent. Once the system of protective molecules becomes inadequate, *e.g.*, owing to evaporation, neighbouring protein molecules may powerfully disturb or actually destroy one another, with the result that their constituent peptide chains are liberated to recrystallise by simple parallel alinement, as described above. If this concept is sound, it means that there are three stages in the life of a non-fibrous protein : (1) the "specific" stage, in which the protein is truly itself (cf. Bonot, *J. Chim. physique*, 1934, **31**, 258); (2) the "denatured" stage, in which its delicately balanced configuration has disintegrated sufficiently to release (or even build up) peptide chains; and (3) the "coagulated" stage, when the peptide chains have aggregated into regular parallel bundles, or crystallites, analogous to the normal form of the fibrous proteins, this last stage being naturally facilitated by thermal vibrations (cf. Lloyd, *op. cit.*, p. 228, for the physicochemical distinction between denaturation and coagulation).

Denaturation by simple self-destruction is not, of course, the only means we can conceive by which the specific configuration of a protein may be overturned; in fact, it is more difficult to think of ways of keeping such complex systems stable : hence the variety of methods by which denaturation may be brought about—by heat, mechanical disturbance, radiation, strong acids or alkalis, etc. But, according to the X-ray interpretation presented here, all methods have this in common, that they lead to the break-up of a particular arrangement of peptide chains characteristic of the protein, and prepare the way for reaggregation in stable parallel bundles. · If the disintegration of the original configuration involves the dissolution of covalent linkages, then we may expect to find in the denatured product certain new radicals not really characteristic of the protein : in particular, if two peptide chains were originally bound together by sharing cystine residues, hydrolytic breakdown of –S–S– linkages would lead to the appearance of –SH groups (cf. Harris, *Proc. Roy. Soc.*, 1923, *B*, **94**, 426 ; Speakman, *Nature*, 1933, **132**, 930).

One final point is noteworthy. In Fig. 4, (1) and (2), and (3) and (4), it will be seen that the side-chain spacing of the albumins, after denaturation, is somewhat less susceptible to water adsorption : and again, in the table, it will be seen that the actual value of the side-chain spacing appears to be rather smaller after denaturation. In other words, not only has denaturation greatly favoured the backbone linkage, but it has also "tightened" the side-chain linkage and decreased its capacity for separation on the entry of water molecules. This also might reasonably be expected from the present standpoint, for the special configuration of an undenatured protein would not necessarily involve the closest possible approach or mutual saturation of the constituent peptide chains : rather would a certain looseness and freedom of active radicals be more probable. Denaturation, on the other hand, would put an end to all that by shaking the chains apart, bringing them into more intimate contact, and effectively masking many of the properties they might otherwise manifest.

193. *Experiments on Hexadeuterobenzene. Part I.*

By G. R. CLEMO and A. McQUILLEN.

THE quantitative preparation of acetylene by the action of water on calcium carbide has been investigated, and a generator of the type A found to be the most effective. An amount of almost pure acetylene corresponding to 60% of the total hydrogen of the water was obtained in this way, and, by heating finally to 500—600° with excess of carbide, 90% of

the theoretical yield, contaminated with some air and methane, could be obtained. The further volume of gas evolved on heating was used separately in the earlier work in order to avoid complications arising from the presence of these impurities.

The literature does not contain any really helpful account of the small-scale polymerisation of acetylene to benzene and much time has been spent in examining this question. The apparatus shown in the diagram is suitable for laboratory experiments. In this part of the work we were greatly helped by Mr. H. G. Dickenson. The acetylene was passed over the catalyst in a heated silica tube, and the distillate collected. Gas-mask charcoal in C was used to absorb the benzene in the earlier experiments, but was abandoned in favour of the receiver (D) cooled in solid carbon dioxide. Several catalysts were tried, including charcoal and tellurium oxide on porous pot (D.P. 547,080; *Zentr.*, 1932, 3113). Carbon had the disadvantage that it required priming by the passage of large amounts of acetylene before it became active, thus confirming the view that finely divided carbon deposited by
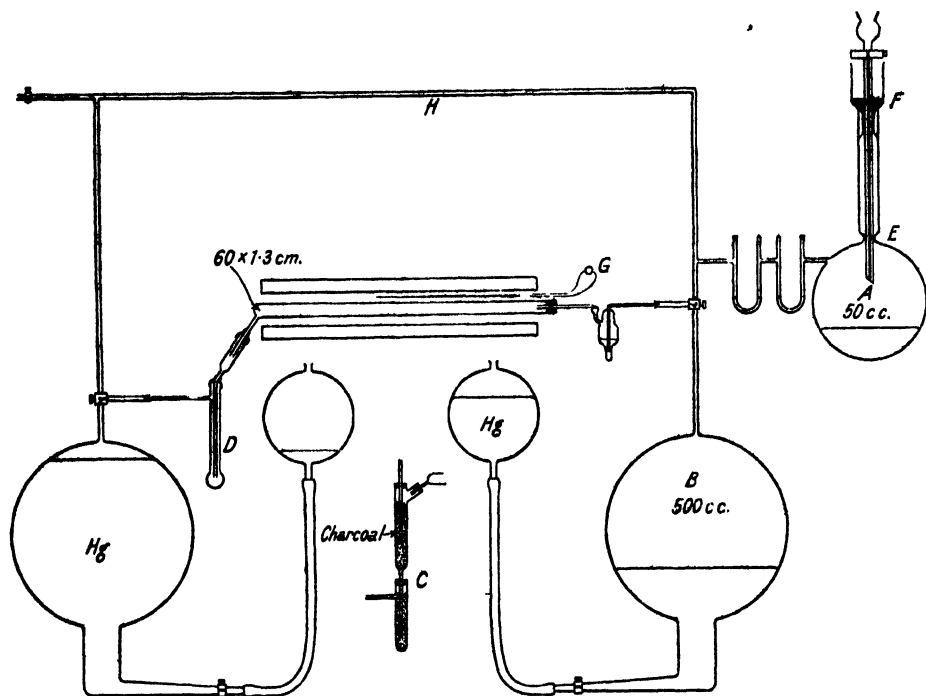
the decomposition of acetylene was the real catalyst (compare, however, Fischer, Bangert, and Pickler, *Brennstoff-Chem.*, 1929, **10**, 279; Zelinski, *Ber.*, 1924, **57**, 264). The optimum temperature for the production of benzene was 650° (Pease, *J. Amer. Chem. Soc.*, 1929, **51**, 3470).

With a tellurium catalyst and carbon dioxide as the carrier gas, complete contraction could be obtained if an "askarite" tube was used in the return circuit at H to remove progressively the carbon dioxide. In all cases 40% of inert gases inhibited further polymerisation. The resultant benzene was contaminated with water, and another oxygen-containing substance which reacted with sodium only at 60°. As the benzene could not be easily purified, it was converted into the *m*-dinitro-compound, of which 80 mg. were obtained from 1·5 g. of water.

When hydrogen was used as the carrier gas, benzene free from oxygen-containing impurities was obtained (yield, 85 mg. from 2 g. of water).

When nitrogen was used, the initial batch of acetylene gave a 50% contraction, but after the discharge of the residual gases (containing the majority of the nitrogen) subsequent

batches gave a 70% contraction. A yield of 0·40 g. of benzene was thus obtained from 2 g. of water.

This work was then repeated with 99% " heavy " water, and a similar yield of dideutero-acetylene (60%) obtained and polymerised. In this case also nitrogen was found to be preferable to carbon dioxide as a carrier gas. A yield of 2·3 g. of liquid distillate was obtained from 10 g. of " heavy " water. This was purified as described in the experimental section and gave 1·3 g. of analytically pure *hexadeuterobenzene*.

The micro-analyses of hexadeuterobenzene were carried out with a furnace and absorption train which had not been used for compounds containing ordinary hydrogen, after extended practice on a similar furnace had given consistent values for ordinary benzene. The results, with C values 6·6 units lower than that for " light " benzene and, with one exception, good values for D, seem to prove the product to be pure hexadeuterobenzene. The value marked $*_2$ was obtained in an ordinary furnace immediately after the C_6H_6 value $*_1$, and it will be seen that the D value is 0·6 low. The H value found for alizarin, analysed next in this furnace, was 0·6 high, the C being quite good.

Nitration of hexadeuterobenzene with " light " sulphuric and nitric acids gave a good yield of a dinitro-compound, m. p. 89°, not depressed by admixture with authentic *m*-dinitrobenzene. The analyses (Table II) do not settle whether exchange has occurred. When the nitration was effected with " heavy " acids,* the dinitro-compound obtained had m. p. 78° and thus it appears that exchange had taken place in the nitration above.

Hexadeuterobenzene has b. p. 82·5° (C_6H_6, b. p. 80·5°), m. p. − 1·0° approx., and $d^{17°}$ 0·954 ± 0·0005.

EXPERIMENTAL.

Generation of Acetylene.—A generator A† was found to be suitable. The three-way tap was adjusted until it was in communication with the reservoir B, which was partially evacuated. A weighed amount of water was introduced into the funnel of A and was added to the carbide drop by drop under a pressure of nitrogen, the carbide being shaken so as to present a fresh surface to each drop. The carbide was passed through a 20-mesh sieve and preheated to 200° to remove any atmospheric moisture. The moist acetylene passed through two U tubes containing carbide and phosphoric oxide respectively. In this way 750 c.c. of either dideutero- or ordinary acetylene could be obtained from 1 g. of the corresponding water.

An additional 380 c.c. of gas containing some 10% of air and methane could be obtained by heating the mixture to 500—600°. In the experiments with " heavy " water the second volume of gas was not generated, the carbide–calcium deuteroxide mixture being stored.

Receivers.—The gaseous benzene could not be collected from the gas stream by mere cooling, for it formed a mist which passed through the receiver. A receiver of the type (C), cooled in ice and packed with absorption charcoal, absorbed this mist, but only some 30% of the benzene could be recovered even by heating the charcoal to a dull red heat in an inert atmosphere. Finally a receiver of the type (D), in which the mist was filtered out by passage through a column of glass-wool, was used successfully. This was cooled in solid carbon dioxide.

Polymerisation of " Light " Acetylene.—(a) *Charcoal catalyst.* The apparatus shown, fitted with the receiver (C), was swept out with carbon dioxide at 700° for 24 hours. Acetylene (1·5 l.) was passed repeatedly (40 times) through the tube containing charcoal (Sutcliffe, Speakmann and Co., H/Q Grade 6—10 Absorption Charcoal) at 650° before any contraction occurred. Acetylene (2 l.) was then passed through the furnace in 500 c.c. batches, each being passed five times. The resultant gases were trapped in (C), packed with absorption charcoal and cooled in ice. Distillation of the charcoal gave a colourless liquid (0·53 g.). This was refluxed with nitric acid (2 c.c.) and sulphuric acid (2 c.c.) for ¼ hour, then poured into water, and the crystalline precipitate filtered off. After recrystallisation from 50% aqueous alcohol, *m*-dinitrobenzene (30 mg., m. p. 89°, mixed m. p. 89°) was obtained (Found : C, 43·1; H, 2·7. Calc. : C, 42·8; H, 2·4%).

(b) *Tellurium catalyst.* Tellurium (2 g.) was dissolved in excess of dilute nitric acid (1 : 4),

* We are deeply indebted to Mr. M. P. Applebey of Billingham for these reagents.

† The long stem of the generator removed the ground joint from the heated zone, the mercury cup seal (F) rendered the use of a lubricant at the joint unnecessary, and the constriction at (E) prevented loss of water in the annular space.

3 K

porous pot sufficient to fill the combustion tube was added, and the whole evaporated to dryness. The tube was filled with the catalyst and ignited at 700° for 48 hours in a stream of carbon dioxide. Acetylene ($\frac{1}{4}$ l.) was collected in B, over mercury, and passed through the furnace six times. An "askarite" tube for the absorption of carbon dioxide was inserted at (H). A colourless liquid (0·25 g.), distilled from the charcoal of the trap, gave *m*-dinitrobenzene m. p. 89°, on nitration. The residual gas (58 c.c.) contained acetylene (65·5%) and carbon dioxide (34·5%).

Polymerisation of Dideuteroacetylene.—The furnace was swept out with oxygen for 24 hours at 700°, no water being collected, and then with oxygen-free nitrogen for a similar period, both gases having been dried by passage through towers of quick lime, calcium chloride, and then phosphoric oxide. Cylinder nitrogen, which contained about 5% of oxygen, was purified by passing up one inclined tube (1 m.) filled with alkaline pyrogallol and a second filled with chromous chloride and amalgamated zinc (Carter and Hartshorne, J., 1926, 363; *J. Soc. Chem. Ind.*, 1926, 474).

0·57 G. of "heavy" water (99%, $d^{20°}$ 1·1051) gave 300 c.c. of dideuteroacetylene, which, after passage five times at the rate of 2 l./hour through the furnace, showed no further contraction. The residual gas (150 c.c.) was discharged from the apparatus.

2·04 G. of "heavy" water gave 1150 c.c. of gas, which was passed in three batches through the furnace. A total contraction of 70% of the original volume was obtained after five passings. The benzene vapour was trapped in a receiver (type D), cooled in solid carbon dioxide. The crude product (0·24 g.) was fractionated, the tail being neglected, and distilled thrice from excess of picric acid (to retain the naphthalene fraction), twice from phosphoric oxide, and finally from sodium. This product was then fractionated, and the middle fraction, b. p. 82·5°, analysed.

A similar experiment with 10 g. of "heavy" water in $\frac{1}{4}$ g. batches gave 2·3 g. of crude distillate, which, after purification, gave 1·3 g. of pure *hexadeuterobenzene*. The analytical results given in Table I were obtained in chronological order.

TABLE I.

| | Ordinary benzene. | | Hexadeuterobenzene. | | |
	C.	H.	C.	D.	N.
Calc.	92·3	7·7	85·7	14·3	0
Found	92·1	7·7	—	—	—
	92·9	7·9	—	—	—
	—	—	85·8	14·8	—
	—	—	86·0	14·7	0
	—	—	86·0	15·45	—
	92·1	8·0	—	—	—
	—	—	86·4	15·2	—
	92·5	8·0 *1	—	—	—
	—	—	85·8	13·7 *2	—
	—	—	86·4	14·8	—
	—	—	86·6	14·7	—

Nitration.—The crude product (0·2 g.) after a two-fold distillation from picric acid was refluxed for $\frac{1}{4}$ hour with concentrated nitric acid (2 c.c.) and concentrated sulphuric acid (2 c.c.), giving 0·31 g. of a crystalline solid, m. p. 89° after three recrystallisations from 50% aqueous alcohol, and not depressed by admixture with *m*-dinitrobenzene. Pure hexadeuterobenzene (0·14 g.) was also nitrated in a similar fashion with sulphuric and nitric deuteracids. After three-fold recrystallisation from petroleum (b. p. 60—80°) a white crystalline solid (0·2 g.), melting at 78° and giving m. p. 87° when mixed with *m*-dinitrobenzene, was obtained. The analytical data obtained are in Table II.

TABLE II.

m-Dinitrobenzene.	C_6D_4 nitrated with "light" reagents.	C_6D_4 nitrated with "heavy" reagents.
Calc.: C, 42·8; H, 2·4; N, 16·7.	$C_6D_4O_4N_2$ requires C, 41·9; D, 4·4; N, 16·3.	
Found: C, 42·5; H, 3·0; N, 16·6%.	Found: C, 42·4; D, 5·1; N, 16·1.	
	42·4; 5·2; 15·7.	
	42·5; 5·3; 15·7%.	
		Found: C, 41·4; D, 4·9; N, 16·5, 16·4%.

NOTES.

Dipole Moment and Structure of Organic Compounds. Part XIV. The Direction of the Electric Moment of the N⫶C Group. By A. WEISSBERGER and R. SÄNGEWALD.

IT has been stated that 4 : 4'-dicyanodiphenyl has an electric moment of $1 \cdot 1D$ (*Helv. Phys. Acta*, 1929, **2**, 257), and from this result the deduction has been made that the N⫶C group is without axial symmetry, *i.e.*, that the direction of its moment does not coincide with the bond joining this group to the benzene ring. The fact that the electric moments of certain aromatic nitriles experimentally determined do not agree with the values which would be predicted by a simple vector addition of the component moments has been considered evidence in support of the same conclusion (*Z. physikal. Chem.*, 1930, B, **10**, 397), although this lack of agreement may well arise from polarisation effects in the attached groups or in the nucleus (*Proc. Roy. Soc.*, 1933, **140**, 562; *Z. physikal. Chem.*, 1933, B, **20**, 151; *Trans. Faraday Soc.*, 1934, **30**, 884).

We thank Dr. C. G. Hampson for an attempt to redetermine the electric moment of 4 : 4'-dicyanodiphenyl. This, however, was not possible because of the low solubility of the compound in benzene at 25° and in decalin at 70°. However, *p*-dicyanobenzene was just soluble enough to be measured in the usual way with benzene as solvent, and the moment has been found to be indistinguishable from zero. It thus appears that the cyano-group shows axial symmetry in accordance with the ordinary model. It would be without analogy if a 4 : 4'-derivative of diphenyl had a moment whilst the *p*-benzene derivative had none. No details on the measurement of the diphenyl compound have been given, and hence it is difficult to suggest the origin of the discrepancy between the earlier result and ours.

p-Dicyanobenzene was prepared according to Limpricht (*Annalen*, 1876, **180**, 89) and recrystallised from alcohol; m. p. 222°. 4 : 4'-Dicyanodiphenyl was prepared according to Ferris and Turner (*J.*, 1920, **117**, 1149). The crude product was sublimed at 190°/0·002 mm. and recrystallised from dioxan and from benzene; m. p. 235—236°.

p-Dicyanobenzene in Benzene (25·0° ± 0·1°).

f_2, %.	d_4^{25}.	ϵ.	n^2.	$P_{1, 2}$.	$P_{1, 2}''$.
0	0·8735	2·272	2·2443	26·610	26·194
0·3780	0·8743	2·274	2·2452	26·672	26·249
0·5183	0·8749	2·275	2·2460	26·696	26·267
0·6625	0·8752	2·277	2·2464	26·726	26·287

$dP_{1,2}/df_2 = 16 \cdot 9$; $dP_{1, 2}''/df_2 = 14 \cdot 2$; $P_2 = 43 \cdot 5$, $P_2'' = 40 \cdot 4$.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, March 8th, 1935.*]

The Structure of Tolan. By ARNOLD WEISSBERGER.

SMYTH and DORNTE (*J. Amer. Chem. Soc.*, 1931, **53**, 1296) found for tolan an electric moment of $1 \cdot 12 D$ and therefore suggested the formula $(C_6H_5)_2C⫶C$. Weissberger and Sängewald (*Z. physikal. Chem.*, 1933, B, **20**, 145), however, stated that the moment of tolan, measured in the usual way, is indistinguishable from zero, and therefore no reason exists to abandon the symmetrical formula established by organic chemists. Berger (*Z. physikal. Chem.*, 1935, B, **28**, 95), as a result of measurements of and deductions from association phenomena, decides in favour of the asymmetrical formula in spite of the absence of a moment. He points out that this may be small, because the moment of *as.*-diphenylethylene is very small (0·5 *D*). I cannot agree with this argument. In the circumstances, however, it seemed worth while to provide *chemical* evidence for one or the other formula. The usual methods of preparation of tolan from *s.*-diphenylethane derivatives are with some reason not considered definite proof, because they may involve rearrangements which are frequent in this group of compounds. However, catalytic reduction of tolan at room temperature can hardly involve a rearrangement of the

skeleton. This has been carried out by Kelber and Schwartz (*Ber.*, 1912, **45**, 1951), dibenzyl being obtained after recrystallisation of the product. Unfortunately the authors state no yield. Their method of reduction was therefore repeated with 0·445 g. of tolan. After 2 hours, the theoretical amount of hydrogen had been absorbed; the solution (acetic acid) was filtered and poured into water and the crystals were collected. The yield was 0·442 g. (99·3% of the theo.) of dibenzyl, m. p. 52·5—53·2°. As *as.*-dibenzylethane is liquid at room temperature, this should be considered definite proof for the symmetrical formula of tolan.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, March 22nd, 1935.*]

The Structure of Glutaryl Chloride. By S. G. P. PLANT and (Miss) M. E. TOMLINSON.

SUBSTANCES hitherto obtained from glutaryl chloride have been derived from its symmetrical form, although the unsymmetrical structure (I) might be responsible for the formation from chlorobenzene of an ill-defined product described by Skraup and Guggenheimer (*Ber.*, 1925, **58**, 2488). It has now been found that both forms are involved in the reaction with anisole and aluminium chloride, the resulting isomeric *αγ-dianisoyl-propane* and *δδ-di-p-anisylvalerolactone* being separated by extracting the latter with aqueous sodium carbonate. Two similarly constituted ethoxy-compounds have been obtained from phenetole, and *γ-anisoyl-* and *γ-phenetoyl-butyric acid* have been prepared for comparison from anisole and phenetole respectively with glutaric anhydride.

$$CH_2 \underset{CH_2 \cdot CO}{\overset{CH_2 \cdot CCl_2}{\Big<}} O \qquad (I.)$$
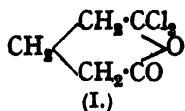
αγ-Dianisoylpropane and its Isomeric Lactone.—A mixture of anisole (14·6 g.), glutaryl chloride (9·3 g.), and carbon disulphide (30 c.c.) was treated with pulverised aluminium chloride (12 g.) and refluxed for 2 hours. After the solvent had been allowed to evaporate, the residue was treated with dilute hydrochloric acid, and any anisole removed in steam. When the sticky residual solid was warmed with aqueous sodium carbonate, *αγ-dianisoylpropane*, colourless needles (3·9 g.), m. p. 99°, from alcohol, remained (Found : C, 73·2; H, 6·4. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·4%), and from the filtered solution dilute hydrochloric acid precipitated *δδ-di-p-anisylvalerolactone* as a sticky mass. It was purified by distillation under reduced pressure and obtained from benzene–petroleum in colourless prisms (3·1 g.), m. p. 111—113° (Found : C, 73·1; H, 6·6%).

By a similar process from phenetole, *αγ-diphenetoylpropane*, colourless needles, m. p. 133°, from alcohol (Found : C, 74·1; H, 7·3. $C_{21}H_{24}O_4$ requires C, 74·1; H, 7·1%), and *δδ-di-p-phenetylvalerolactone*, colourless prisms, m. p. 82°, from benzene–petroleum (Found : C, 73·8; H, 6·9%), were obtained. Both lactones were readily dissolved by cold aqueous sodium carbonate.

γ-Anisoyl- and γ-Phenetoyl-butyric Acid.—When glutaric anhydride was allowed to react with anisole under conditions similar to those described above, the product, after removal of the volatile material in steam, was entirely soluble in aqueous sodium carbonate. *γ-Anisoyl-butyric acid*, practically colourless prisms, m. p. 137°, from alcohol, was then precipitated from the solution by the addition of hydrochloric acid (Found : C, 65·1; H, 6·3. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%). Prepared similarly from phenetole, *γ-phenetoylbutyric acid* separated from benzene in almost colourless prisms, m. p. 114° (Found : C, 66·2; H, 6·6. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%).

The authors are grateful to the Chemical Society for a grant.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, May 11th, 1935.*]

2-Iodo-3-Hydroxybenzoic Acid. By THOMAS A. HENRY and THOMAS M. SHARP.

SOME years ago the authors described an iodo-3-hydroxybenzaldehyde in which the position of the iodine was uncertain (J., 1922, **121**, 1059). This aldehyde on oxidation with permanganate in acetone yielded a minute amount of a substance, m. p. 133° (in error this was given as 233° in the paper), which was assumed to be the corresponding iodo-3-hydroxybenzoic acid. It was subsequently shown by two other methods (J., 1924, **125**, 1051) that the aldehyde in question was 2-iodo-3-hydroxybenzaldehyde, so the substance produced on oxidation should have been 2-iodo-3-hydroxybenzoic acid. As this acid would be expected to have a higher melting point than 133°, and there are numerous instances on record of failure to oxidise aromatic hydroxy-aldehydes to the corresponding acids (*e.g.*, Tiemann, *Ber.*, 1876, **9**, 415; Brady and Dunn, J.,

1915, 107, 1959), the authors have thought it advisable to repeat the previous observation and to effect the oxidation by another method.

Repetition of the direct oxidation of 2-iodo-3-hydroxybenzaldehyde with permanganate in acetone gave again a minute yield of crystalline substance, m. p. about 133°, which has proved to be merely impure recovered aldehyde (m. p. 159—160°), and no acid could be isolated. The required acid has now been obtained in small, though sufficient yield, by oxidation of the acetyl derivative of the aldehyde, followed by hydrolysis.

2-Iodo-3-hydroxybenzaldehyde (2 g.) was boiled for 1 hour with acetic anhydride (10 c.c.), and the excess of reagent removed under reduced pressure. The oily acetyl derivative was dissolved in acetone (25 c.c.) and treated with potassium permanganate (2·4 g.), added in small quantities. The solution quickly became decolorised : the manganese dioxide was filtered off, suspended in water, and decomposed with sulphur dioxide. This furnished a small amount of acid (0·4 g.). The acetone filtrate on evaporation left an oil, which was extracted with 5% sodium bicarbonate solution. The alkaline solution, after acidification, yielded to ether a further quantity of acid (0·41 g.), whilst unoxidised aldehyde remained undissolved by the bicarbonate. This portion was again oxidised with permanganate in the same manner, and the unoxidised portion treated similarly a third time. In this way there were finally obtained 1·27 g. of 2-*iodo-3-acetoxybenzoic acid*, which crystallised from benzene in colourless needles, m. p. 179—180° (corr.) (Found : C, 35·55; H, 2·4; I, 41·5. $C_9H_7O_4I$ requires C, 35·3; H, 2·3; I, 41·5%). On hydrolysis with 5% alcoholic potassium hydroxide, the acetylated acid was converted into 2-*iodo-3-hydroxybenzoic acid*, which formed colourless needles from chloroform, m. p. 158—159° (corr.) (Found : C, 31·9; H, 1·9; I, 48·2. $C_7H_5O_3I$ requires C, 31·8; H, 1·9; I, 48·1%). The melting point was depressed to 135° on admixture with 2-iodo-3-hydroxy-benzaldehyde. It is noteworthy that the m. p. of the acetyl derivative is higher than that of the free hydroxy-acid, whereas the m. p.'s of the other two known iodo-*m*-hydroxybenzoic acids are higher than those of the corresponding acetyl derivatives (3-hydroxy-4-iodobenzoic acid, m. p. 226°, acetyl derivative, m. p. 203°; 3-hydroxy-6-iodobenzoic acid, m. p. 198°, acetyl derivative, m. p. 157°. Brenans and Prost, *Compt. rend.*, 1924, **178**, 1285).—WELLCOME CHEMICAL RESEARCH LABORATORIES, LONDON, N.W.1. [*Received, April 11th, 1935.*]

Validity of Holden and Lapworth's Theory of the Mechanism of Abnormal Michael Additions.
By C. K. INGOLD and H. N. RYDON.

MICHAEL and Ross, reviving an early idea due to Thorpe, advanced the view that sodioalkyl-malonic esters may undergo partition in the sense R—·CNa(CO₂Et)₂ during addition to un-saturated esters in the presence of an equivalent of sodium ethoxide (*J. Amer. Chem. Soc.*, 1930, **52**, 4600). Holden and Lapworth pointed out that this unorthodox assumption is unnecessary, and that every such apparent partition can be explained as a normal addition, followed by a change of structure due to Claisen condensation and alcoholysis (J., 1931, 2370).

Very recently one of us (H. N. R.) recommended a return to the hypothesis of Michael and Ross, on the ground (this vol., p. 420) that the actual product (shown to be II) from ethyl sodiobenzylmalonate and ethyl fumarate, and the normal addition product (I) (which can be prepared in an independent way) yield stereoisomeric, rather than identical, acids on hydrolysis (Duff and Ingold, J., 1934, 87). It is argued that different acids (III and IV), having two asymmetric carbon atoms (β and γ), cannot both be formed through a single ester (I), having only one (β), as Holden and Lapworth's mechanism requires.

(⟶ observed transformations. $\xrightarrow{\text{(H.L.)}}$ Holden and Lapworth's theory.)
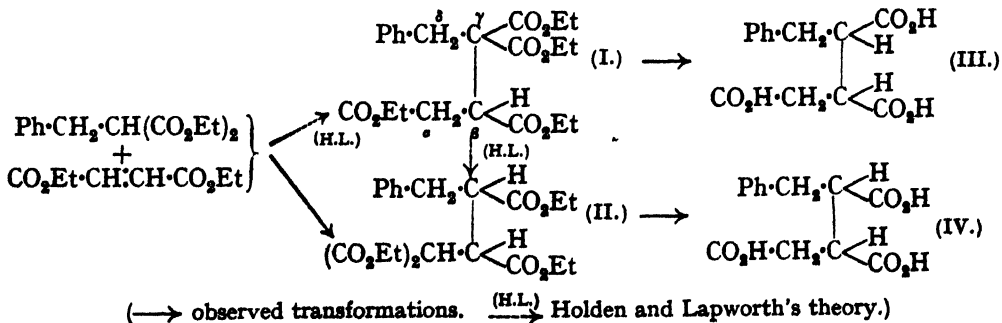
The writers desire to point out the following. The two γ-carbethoxyl groups of (I) are distinguishable inasmuch as, when the chain αβγδ is coplanar, one is " *cis-* " and the other " *trans-* " with respect to the β-carbethoxyl group. If the changes (I) ⟶ (III) and (I) ⟶ (II) involve the loss or displacement of different γ-carbethoxyl groups, and the numbers of Walden inversions in the two changes are equal (both one, or both zero), then the final acids will be stereoisomeric. Alternatively, if the two changes involve the same carbethoxyl group, but the numbers of Walden inversions differ by unity, then the final acids will still be stereoisomeric. There are thus various ways in which the observations can be accommodated to Holden and Lapworth's theory, which appears to be still acceptable.—UNIVERSITY COLLEGE, LONDON, W.C.1, and IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, May 2nd, 1935.*]

OBITUARY NOTICES.

LEONARD ARCHBUTT.

1858—1935.

LEONARD ARCHBUTT, F.I.C., was born on April 2nd, 1858, at Ovington Square, London, and was the son of Samuel Archbutt, a solicitor. Educated at private schools and University College, he was articled to the late A. H. Allen of Sheffield, and later became his chief assistant. Entering the service of the Midland Railway in 1881, he remained as Chief Chemist till he retired in 1923, the latter portion of his service being with the L.M.S. after the amalgamation of the railways. His death took place suddenly on April 28th, 1935.

Archbutt has been fittingly described as the greatest of railway chemists. He was life member of the Chemical Society, the Institute of Chemistry, the Society of Public Analysts, and the Society of Chemical Industry. Of the last-named, he was an original member, served on the Council and Committees, and was twice chairman of the Nottingham section. In the *Journal* of that Society he published eleven papers, chiefly on oils, fats, and grease, but including the determination of sulphur in steel and of minute quantities of arsenic in coke. He was President of the Society of Public Analysts, 1912—13, being the first chemist other than a public analyst to occupy that position. He contributed many papers and notes to the *Analyst* between 1884 and 1913, among them being contributions on " Estimation of Oxygen in Copper " and on water-testing.

An original member of the Institute of Metals, Archbutt served on the Council from 1911 till 1924, and frequently contributed to the discussions. Two of his papers on " The Influence of Certain Elements on the Forging Properties of Copper at a Red Heat " (*J. Inst. Mets.*, 1912, **7**, 262) and on " A Curious Change in the Microstructure of White Metal produced by Traces of Zinc " (*ibid.*, p. 266) anticipated work which has since been published elsewhere. He served on the Corrosion Committee from 1911 to 1924. Important pioneer work on the failure of lead sheathing of electric cables was also published by the Faraday Society (*Trans.*, 1921, **17**, 22).

Archbutt was active at the Railway Clearing House, and was a member of the Goods Managers Committee on Explosives and other dangerous goods from 1893 till his retirement in 1923. He was elected Chairman of the Committee of Chemists and served from 1894 till 1905, also in 1913, and from 1920 to 1923, a total of sixteen years. For services on the Standing Committee, respecting conveyance of explosives, for H.M. Government during the war, he was awarded the O.B.E., but declined the honour on the grounds that he had done no more than his duty.

Reference has already been made to Archbutt's interest in oils and greases, and to water treatment. He was joint author of a standard treatise on " Lubrication and Lubricants," published in 1899 (Griffin and Co.), now in its fifth edition, and joint inventor of the Archbutt–Deeley water-softening process which has been largely used. He was also joint author of a paper on " The Thermo-dynamics of the Automatic Vacuum Brake " (*Engineer*, 1890, **69**, 509; **70**, 21). He was interested in local technical education, serving on the Derby Education Committee and as Chairman of the Derby Society of Engineers. He lived to enjoy some years of retirement after a long and active career. At the time of his retirement the chemical laboratory at Derby was probably the best equipped railway laboratory in this country, if not in the world.

A man of modest and retiring disposition, Archbutt inspired confidence and friendship in those with whom he was associated. His advice was often sought and freely given, and his skill, industry, and character did much to raise the status of railway chemists. Many will deplore the passing of an old friend and valued colleague.

THOMAS TURNER.

JAMES MUNSIE BELL.

1880—1934.

PROFESSOR JAMES MUNSIE BELL, Dean of the School of Applied Science, University of North Carolina, U.S.A., who died on March 3rd, 1934, was born in Chesley, Ontario, Canada, on April 19th, 1880. At the University of Toronto from 1898—1903, he successfully carried at the same time honour courses in Chemistry, Physics, and Mathematics, and was awarded the degrees of B.A. and M.A. At Cornell University he held the Sage Fellowship in Chemistry and obtained the degree of Ph.D. For the next five years he worked at the U.S. Department of Agriculture on physicochemical problems in the genesis of soils, reclamation of alkali soils, and fertiliser, the results of these researches being recorded in a number of governmental publications and journal articles.

Coming to the University of North Carolina in 1910, Bell became Head of the Department of Chemistry in 1921, although during the war he served overseas in the Chemical Warfare Service of the United States. He was again in England and Germany in 1926—1927, as Kenan Travelling Professor. His published investigations relate to heat capacities and other properties of the nitrotoluenes, to concentration cells, free energy, copper salts, and other problems. He is more widely remembered perhaps by his work on the compounds of zirconium, part of which was done in collaboration with Dr. Venable. He led a full academic life as investigator, influential teacher, scholar, and administrator. It was for his warm human personality and influence that Bell was most esteemed in the life of the college community. He made a substantial contribution to the establishment of the educational and administrative ideals and policies of the university.

He was elected a Fellow of the Chemical Society in 1925.   J. W. McBAIN.

GIUSEPPE GRASSI CRISTALDI.*

1860—1934.

CATANESE by birth, Giuseppe Grassi Cristaldi belonged to the group of students whom Stanislao Cannizzaro gathered round him in the period of his greatest activity and directed to the study and teaching of science at a time when, largely by his influence, the importance of chemistry in education and in the life of the nation was beginning to be appreciated in Italy.

After graduating in his native town, Giuseppe Grassi took his degree in chemistry in Rome under his great master in 1888, and remained there as assistant till 1895, when he went to Catania as Professor Extraordinary. Becoming full professor in 1900, he remained at Catania without interruption until his death on 20th December, 1934.

There his life was dedicated to the development of the school of chemistry. Though specially interested in organic chemistry, he did not neglect other branches, and his enthusiasm for keeping abreast of the progress of science in widely separated fields left him perhaps but too little time for laboratory research, for which in the earlier part of his career he had shown much capacity.

His first researches were on the problem of santonine, which occupied the school of Cannizzaro from 1874 onwards with results of much importance to the knowledge of its constitution. He was first engaged on the reduction products of santonine—santonone, *i*sosantonone, the santoninic acids, and their oxidation products. He studied also the reduction products of iposantoninic acid and the structure of some of its derivatives. Other work was on the synthesis of benzoglyoxaline, the formation of trioxymethylene by the decomposition of chloroacetic acid by heat, and the constitution of hexamethylenetetramine, for which he believed he confirmed the formula of Losekahn. He worked also on problems of local importance, the analysis of waters and of the material thrown up by the

* Compiled from the obituary notice by Professor B. L. Vanzetti in *La Chimica e l'Industria* (1935, **17**, 48).

great volcano, in which he, like every good citizen of Catania, had a passionate interest. But his principal life work was his teaching and particularly the thorough instruction in laboratory work which he imparted to all his students.

Greatly esteemed by the Academic body for his uprightness of character and serenity of disposition, he occupied many important posts in the University and carried out much valuable work for the City and Province.

The appearance of health which he preserved to the end did not betray the serious malady affecting his last years. He was fully conscious of his condition, but determined not to spare himself. His last lecture was delivered on December 19th, and on the morning of the 20th a sudden heart attack ended his life while still in service.

He was born in 1860 and is survived by his wife and daughter.

A. H. BENNETT.

WILLIAM THOMAS GENT.

1855—1934.

WILLIAM THOMAS GENT was born in Macclesfield in 1855. He was educated at the Grammar School in that town, subsequently entering Berlin University as a student under Professor Rammelsberg.

On his return to England in 1874, Gent was employed as Chemist by the Widnes Metal Co., which was under the direction of Muspratt, Claudet, and others, and while there he came into contact with many prominent chemists, including Brunner, Mond, Carey, and Norman. With these he was instrumental in forming the local branch of the Society of Chemical Industry. His personality and ability attracted the attention of Richard Morris, who engaged him as Chemist at his Chemical Works at Misterton, where Gent remained for close upon 50 years, subsequently filling the position of Manager, and finally becoming a partner.

Gent held numerous public offices, including that of Chairman of the Parish Council and of the Misterton Rural District Council from its inception until 1925. He served on the School Board, was the founder of the Victoria Institute at Misterton, and was connected with many other charities. His public services were recognised by his appointment as a Justice of the Peace for the County of Nottingham in 1909, and he sat regularly on the Bench at Retford.

Apart from his activities in business and public life, Gent had two hobbies—travel and photography. He was a Fellow of the Royal Geographical Society and travelled widely, leaving behind him a valuable photographic record of the many countries he had visited. He formed a wide circle of friends, and during his student days at Berlin was on intimate terms with the Mendelssohn family; he ever cherished the memory of the musical evenings at which he was privileged to be present.

Gent retired from business in 1925, and spent the remaining years of his life at Bexhill-on-Sea, where he died on November 27th, 1934, at the age of 79. He was elected a Fellow of the Society on April 17th, 1879.

ARTHUR WILLIAM NUNN.

1867—1935.

ARTHUR WILLIAM NUNN, who died on January 25th, belonged to an old Colchester family and he received his early education at the local Grammar School. He, or his parents, chose pharmacy for his career and he was therefore apprenticed to a Mr. Arthur Weddell; in 1888 he passed the Qualifying Examination and five years later obtained his Diploma as a Pharmaceutical Chemist. For some years he was on the staff of Burroughs, Wellcome & Co., but in 1907 he opened his own pharmacy in Crouch Street, Colchester, where he was joined in 1925 by Mr. A. R. P. Sherry, Ph.C. For two years, 1918—1920, he was an

examiner for the Pharmaceutical Society, and he conducted classes in botany and other subjects at Colchester Technical School.

Nunn contributed, in pre-war days, a number of articles on galenical pharmacy to *The Pharmaceutical Journal.* In 1912, he put forward an alternative method of preparing extract of belladonna in order to avoid the hygroscopic nature of the pharmacopœial preparation, and at an earlier date (1909) he suggested the use of a " Sparklet " syphon for making solution of magnesium bicarbonate. His interest in apparatus is shown by his description in 1910 of a portable apparatus for the preparation of hydrogen sulphide and in 1919 of a capsule for regulating the temperature of bacteriological incubators and drying cupboards.

Nunn played an active part in local affairs; he was a town councillor and his work on the Health Committee was particularly valuable because of his technical ability and sound knowledge of economics. He leaves a widow and two daughters.

E. T. NEATHERCOAT.

SVEN LUDVIG ALEXANDER ODÉN.

1887—1934.

SVEN LUDVIG ALEXANDER ODÉN was born in Norrköping, Sweden, on April 6th, 1887, and died in Stockholm on January 16th, 1934. He came of an old Swedish family, among the members of which had been farmers, clergymen, and public functionaries. His father was a captain in the army. After having received school education in his home town, he came to Upsala University, where he obtained his doctor's degree in 1913. Here he continued his research work for several years, at the same time lecturing in chemistry. In 1920 he was appointed professor of inorganic chemistry in the Institute of Technology, Stockholm, a position which he exchanged for the directorship of the Chemical Department of the Agricultural Research Station at Experimentalfältet near Stockholm in 1925.

Odén started research work in a laboratory where colloid chemistry was one of the main subjects of interest. At that time (1909) Zsigmondy's discovery of the inhomogeneity of colloidal solutions and Wo. Ostwald's generalisations on disperse systems had rendered thorough investigations of well-defined colloids highly desirable. Odén undertook a careful study of the sulphur hydrosols and succeeded in analysing these complicated colloids in a masterly manner. The influence of degree of dispersion on the properties of the sols was measured quantitatively after he had fractionated the polydisperse original sulphur sols into a series of practically monodisperse sols. His monograph on colloidal sulphur is a classic.

The problem of polydispersity occupied Odén's mind a good deal during the following years. He was looking for ways and means of determining size-distribution curves of disperse systems. In the case of colloidal sulphur, fractional coagulation had enabled him to get a rough idea of the size-distribution. Odén was not content with this—in his own opinion—rather incomplete result. He wanted to solve the problem in a more general way. The rate of settling of suspended particles is, for a certain material, a function of their size and shape, or simply of their equivalent radius, as Odén put it. He devised an automatically recording balance and worked out the theory for the calculation of size-distribution curves from the accumulation of sediment on a plate immersed in the suspension. By means of this apparatus he studied the formation of various precipitates and measured the size-distribution of clays.

His first records of the distribution of clay-particles demonstrated the far-reaching possibilities of this new research tool, the automatic balance. Odén had the power of looking at things with a bird's-eye view, he possessed that faculty of connecting seemingly disparate phenomena which is a characteristic of the genius. By applying his method of quantitative size-analysis to various kinds of soil, he was able to bring a number of important geological and agricultural questions nearer to their solution. His methods were elaborated in more detail during a stay at Rothamsted in 1923, where he enjoyed the collaboration of a number of distinguished English research workers.

During his boyhood days Odén had taken a great interest in botany, and now his method for size-distribution measurements brought him into the field of agriculture. When the chair of director at the chemistry department of the Experimental Station became vacant, he applied for it and received the post as a matter of course. Here he worked for nine years on various problems of plant biochemistry such as the nutrition capacity of different soils, and the physiology of assimilation, especially as regards the artificial illumination of growing plants. The way in which he attacked these problems showed the remarkable originality of his mind.

During Odén's Upsala years the writer had the privilege of being closely associated with him. Many a night we spent together in discussing the problems of disperse systems. But Sven Odén was not merely the scientist. He took a deep interest in literature and arts as well as in the living things of Nature. We hunted rare books and rare flowers together. In these pursuits he showed the same overflowing vitality as in his scientific researches. He read much and became a connoisseur not only of Swedish but also of English and French literature. Sven Odén was a man of many interests but above all he was an indefatigable and restless seeker. To him had been granted the unusual gift of combining intuitive imagination with hardy perseverance.   THE. SVEDBERG.

ALLAN WINTER ROWE.

1879—1934.

THROUGH the death of Allan Winter Rowe at Boston, Massachusetts, last December, medical science has lost the services of a chemist who for 20 years had been working with great energy and marked success upon the chemical aspects of disorders of the ductless glands.

The following details of Rowe's career have been taken from the obituary notice which appeared in January in *Bostonia*. His English friends, most of whom knew him as a young man, will not be surprised that he accomplished so much, and so brilliantly fulfilled his early promise. With them will remain the memory of a man of sterling character, unsparing of himself in any cause he adopted, a lover of fair play, and a charming companion in social life.

Rowe at the time of his death was Professor of Chemistry at the Boston School of Medicine and Director of Research at the Robert Dawson Evans Memorial for Chemical Research and Preventive Medicine. His connection with both of these institutions was a long one—he began as lecturer in the former in 1906, was appointed Research Associate at the Evans Memorial in 1910, and became Director in 1921.

It was at the Evans Memorial that Rowe found ample scope for the employment of those qualities which he possessed in large measure—energy, wide knowledge of his own and allied subjects, lucidity of thought and expression, and the power of inspiring others. That under his direction research work progressed rapidly is shown by the growth of his staff and the number of his publications. During the period January 1929 to June 1934 there appeared forty-seven papers of which he was the sole or joint author; his monograph " The Differential Diagnosis of Endocrine Disorders " appeared in 1932.

In 1933 Rowe was chosen as President of the Society for the Study of Internal Secretions and subsequently Chairman of the Council. He was Vice-President and Trustee of the Memorial Foundation for Neuro-Endocrine Research, and was on the editorial staff of *Endocrinology*. Evidence of the recognition which his services to medical science had gained is reflected in his election to membership, or honorary membership, of numerous medical organisations. He was also a member of many chemical and scientific societies at home and abroad.

Much might be written of Rowe's services to the cause of education in general, but it will suffice to quote what was said of him by the President of Norwich University (Rowe was a member of the University Court). " In him were combined, in a finer and

greater degree, every quality of broad character, scholarship, sportsmanship, leadership, and human understanding of the individual and general needs of an educational institution than in any man that I have ever known."

Rowe's love of athletics never waned, and he took an active part in the development of University sport in various directions, being at one time a member of the A.A.U. Olympic Committee.   Unable to undertake active service during the war, owing to an imperfectly healed fracture of the ankle, he was prominent in the organisation and maintenance of Base Hospital 44, which came to be regarded as a model unit.   W. GOODWIN.